Assembly of Ion Channel Mimics from a Modular Construction Set

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Ion channel mimics were assembled from a modular construction set consisting of *core units*, derived from polycarboxylate 18-crown-6 ethers, *wall units*, derived from macrocyclic tetraesters, and *polar head groups* which provide overall amphiphilic character. The preparation of symmetrical and side-discriminated macrocyclic tetraesters from diols and maleic anhydride gave the required macrocycles in low yields by acid-catalyzed esterification, or by carboxylate alkylation. Addition of 1 equiv of 3-mercaptopropanol to the macrocyclic dienes gave the wall unit precursor. Coupling of the walls to the crown ether via esters was achieved by carboxylate alkylation. The syntheses were completed by Michael addition of head group thiolates. Twenty-one candidate ion channels of molecular weight 1600–4800 g/mol were prepared and characterized.

Transmembrane ion channels are essential to key life processes: energy production, energy storage and transduction, signal propagation, and signal processing.[1] Natural ion transporters are large protein aggregates containing multiple transmembrane segments which act in concert to control transmembrane ion and potential gradients. Structural information is now emerging from molecular biology,[2] but much of the molecular scale detail has been inferred from low molecular weight ionophores such as gramicidin[3] or amphotericin.[4] These sources suggest that artificial channels for the transport of ions across bilayer membranes could be designed according to the following principles: (i) A channel would have a polar core surrounded by a nonpolar exterior layer for simultaneous stabilization of an ion in transit and favorable interaction with membrane lipids; (ii) a channel would have the overall length and shape to fit into a bilayer membrane approximately 40 Å thick. Criterion ii forces attention on the synthetic task as it defines a minimum molecular weight of 3500–4000 g/mol for a functional structure (cf. gramicidin dimer, 3740 g/mol).[3]

Functional artificial ion channels have been reported which illustrate the general criteria. The most obvious course is to prepare oligopeptides with high helical content.[5] Other reported systems are based on cyclodextrin,[6] polymeric crown ether,[7] and "bouquet" shaped crown ether and cyclodextrin motifs.[8] One of the most active systems is a simple tris-crown ether derivative reported by Gokel for the transport of sodium ion.[9] All of these systems envisage a uni- or bimolecular transmembrane structure, similar to the gramicidin structural paradigm. Alternative systems based on multicomponent aggregates, akin to an amphotericin pore, have also been explored.[10] Some time ago we reported the synthesis and activity of a functional ion channel[11] and preliminary mechanistic work[12] which established the channel-like behavior of one compound. This paper reports the synthesis of a suite of compounds of the same type. A structure–activity approach to the elucidation of mechanism will be reported separately.[13]

Our design proposal is sketched in Figure 1. We envisaged a "core" unit lying near the bilayer mid-plane with "wall" units radiating from it. The core unit would provide a rigid frame to direct the wall units to the face of the bilayer. The wall units themselves would be fairly stiff to provide structural control and would incorporate both the polar and nonpolar functionality required for a channel. The structure would be completed with hydrophilic "head" groups to provide overall amphiphilic character and to assist in the transmembrane orientation of the molecule. Our choice for the core units are polycarboxylate crown ethers derived from tartaric acid. A series of di-, tetra-, and hexacarboxylic acid derivatives of 18-crown-6 from either (*R,R*)- or *meso*-tartaric acid is readily available.[14] When (*R,R*)-(+)-tartaric acid units are incorporated into 18-crown-6, they reinforce the conformational preference for *gauche* torsion angles of

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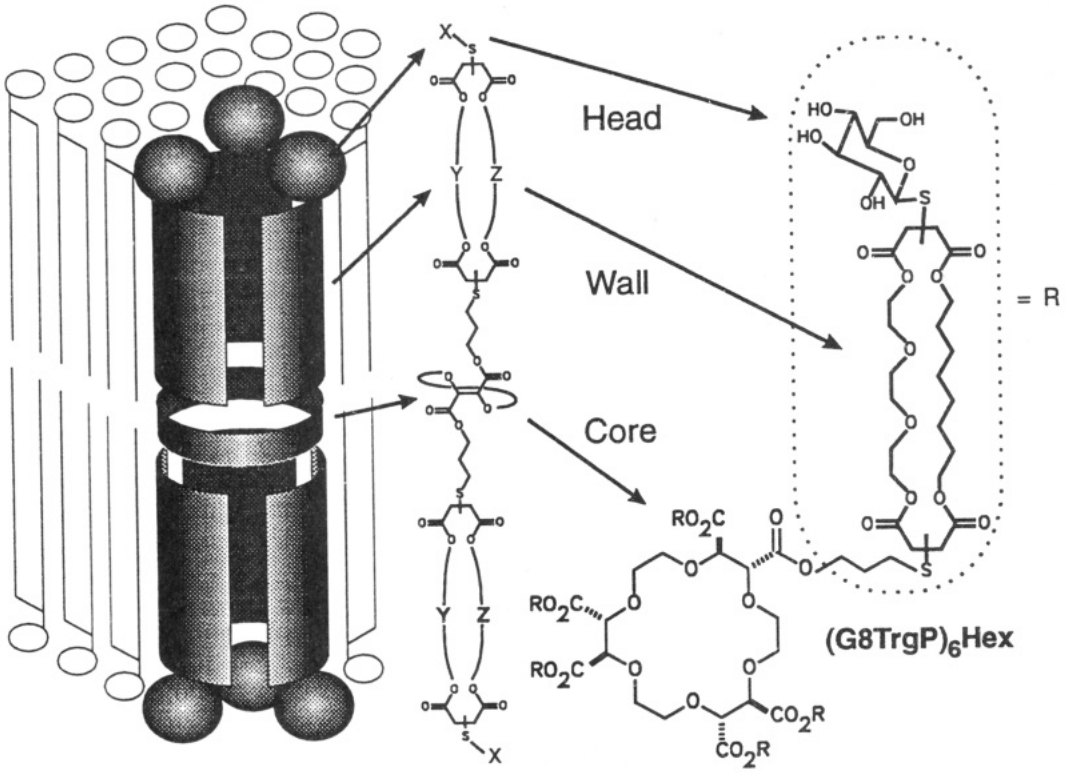

Figure 1. Design proposal for ion channel mimics. Generalized structure indicates possible structural variation of groups X, Y, and Z; complete structure offers one possibility: Y = $-(CH_2)_8-$, Z = $-CH_2CH_2OCH_2CH_2OCH_2CH_2-$, X = glucose.

the OCH_2CH_2O units.[15] This results in well-defined conformations in which the crown ether is held open and the carboxylate groups point perpendicularly to the mean plane of the macrocycle.[16] Linkage of wall units to the crown ether core could be via either esters or amides of the carboxylic acids.[17] The series of di-, tetra-, and hexa-substituted crown ethers would then act as two-, four-, and six-spoke core units.

The wall units chosen are macrocyclic tetraesters derived from maleic anhydride. As reported by Fuhrhop,[18] the intermediate macrocyclic dienes undergo facile Michael additions with sulfur nucleophiles to form two-headed amphiphiles (bolaamphiphiles) capable of forming thin monomolecular membranes. The literature data, together with model building and molecular mechanics explorations, suggest that the macrocycles could adopt the oblong shape pictured in Figure 1. The wall units need to extend about 15 Å: the tetraester derived from 1,8-octanediol would be about the correct length. Side-discriminated tetraester macrocycles bearing polar and nonpolar functional groups (**Y**, **Z**) would provide the necessary functionality, but were not known at the outset.

The target structures are large and amphiphilic and we anticipated difficulties in purification. A precursor lacking the head groups would still be large but would not be amphiphilic. We therefore envisaged head group addition via a Michael reaction as the last step with the hope that high unit efficiency would facilitate final purification. The link between the wall and the core also uses Michael addition to the wall unit. Of several choices ($(CH_2)_n$, amide, ester), we settled on a propyl spacer to an ester linkage created by carboxylate alkylation as the most reliable combination (*vide infra*). The synthetic plan is summarized in Scheme I.

Given the number of combinations possible and the complexity of the structures, we were forced to use a semisystematic naming system to track the large number of similar products at hand. Names and substructures are equated in Figure 2. Each synthon was assigned a simple letter or number name: **G** = 1-mercapto-β-D-glucose,[20] **P** = 3-mercaptopropyl, 8 = from 1,8-octanediol, **Trg** = from triethylene glycol, **Hex** = the hexacarboxylate crown ether $18C6A_6$, etc. (See Appendix for comprehensive list of compound name abbreviations.) Each intermediate was named as a combination of its synthon abbreviations with the exception that the maleate esters are implied: 8_2 = the macrocyclic tetraester from 2 mol of 1,8-octanediol (and 2 mol of maleic anhydride), **8Trg** = the macrocyclic tetraester derived from 1 mol of 1,8-octanediol and 1 mol of triethylene glycol (and 2 mol of

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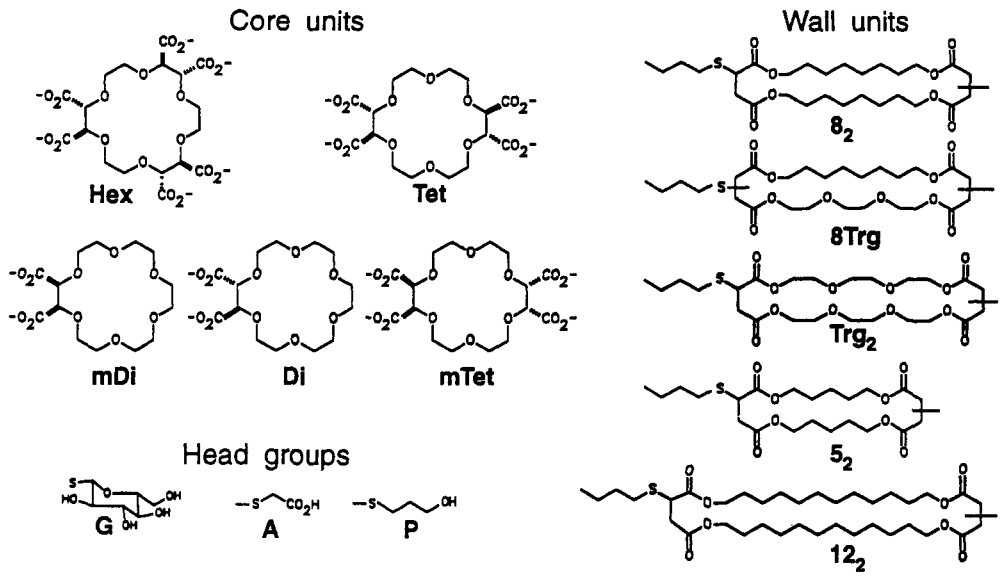
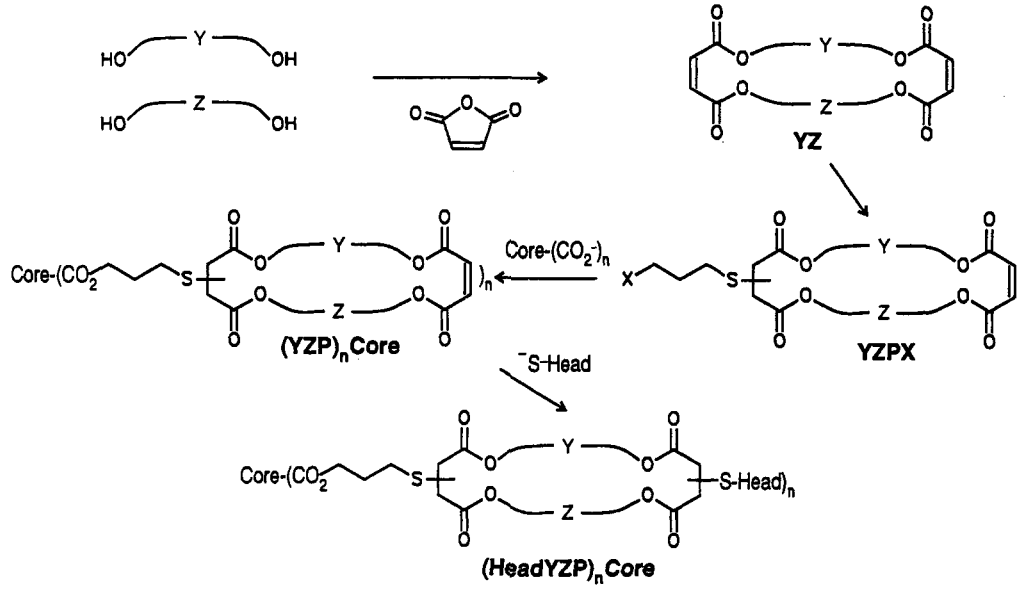


Figure 2. Components of the modular construction set. See text for naming conventions.

Scheme I



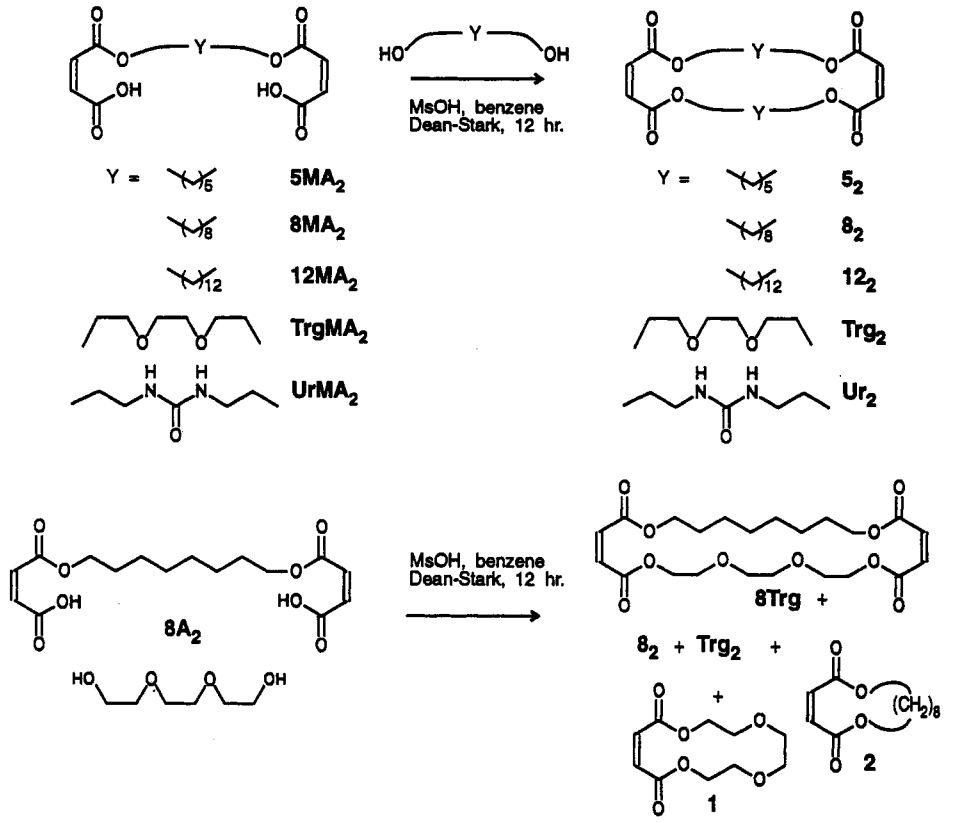
maleic anhydride), etc. The final structures were ordered from head to core: (head + wall + spacer)$_n$ + core. Thus **(G8TrgP)$_6$Hex**, as illustrated in Figure 1, is a thioglucose head group + a tetraester wall unit derived from 1,8-octanediol and triethylene glycol + a propyl spacer, as the hexakis ester of the 18C6A$_6$ crown ether. The naming convention does not attempt to keep track of the regio- and stereoisomers, hence **8Trg** could refer to a *cis,cis*-isomer (as in Scheme II), or to a *trans,trans*-isomer (as in Scheme III). The regio isomers of more complex products are also ignored by the naming scheme.

Figure 2 illustrates the components of a modular construction set, or molecular tinkertoy,[19] which have been prepared and which are consistent with the synthetic plan. The final assembly process involves only two types of reactions which have been optimized to permit assembly of any of the potential combinations. The core units offer choices of two, four, or six points of attachment with two types of conformational control: the axial orientation of Figure 1 from (*R,R*)-tartaric acid, and a distorted conformation from the *meso* derivatives **mDi** and **mTet**.[14] The wall units offer a range of lengths and polarities, and the head units vary in size, charge, and hydrophilicity. We report 21 of the 75 combinations to illustrate the generality of the approach and to provide materials for a structure–activity study.[13]

Results and Discussion

Synthesis of Macrocyclic Tetraester Wall Units. The macrocyclic tetraesters were prepared from maleic acid and diols by acid-catalyzed esterification as outlined by Fuhrhop[18] (Scheme II). The reaction can be done in two steps, or in a single pot without isolation of intermediate diacids **YZA$_2$**. The symmetrical macrocycles with $(CH_2)_n$ chains (**8$_2$**, **5$_2$**, and **12$_2$**) were simple to isolate by crystallization in yields of 10–15%. The more polar symmetrical derivatives required chromatographic separation to give **Trg$_2$** in 7% yield and **Ur$_2$** in only 2% yield. The drop in yield with the polarity and hydrogen bonding capability of the diol is completely general and limits the types of functional groups which can be incorporated by this route.[21] The macrocycle **Ur$_2$** and other examples containing amide functional groups are formed in cases

Scheme II



where the diol is sufficiently soluble, but their yields are too low for practical use in the subsequent steps.

Acid-catalyzed esterification to form side-discriminated marocyclic tetraesters such as **8Trg** gave statistical mixtures of all the transesterification products (Scheme II). Isolation of **8Trg** by chromatography is complicated by its coelution with the 1:1 macrocycle **1** under all conditions explored and by the identical chemical shifts in the ^{1}H NMR spectrum of **8Trg** and **1**. The two can be distinguished by slightly different ^{13}C NMR signals of the olefinic carbons and can be separated by distillation to remove the more volatile **1**, followed by **8Trg**. Direct distillation from a crude reaction product is not possible, so a chromatographic step to give fractions enriched in **8Trg** but with different volatile (**1** and/or **2**), and involatile impurities (**Trg$_2$** and/or polymer) is required. Separate distillation of the fractions gives **8Trg** in a combined yield of 5–7%.

Macrocyclic tetraesters can also be prepared by carboxylate alkylation (Scheme III). There is no competing transesterification in these cases, but the yields are no better (**8Trg**: 7%; **8Phg**: 3%; **8Ur**: 0.2%). The conditions are compatible with a range of amide-containing materials, so the low yields must reflect inefficient ring closure. In some cases trace I_2 provokes *cis* to *trans* isomerization of the maleate units.

The mono-adduct formation by Michael addition of 3-mercaptopropanol to the macrocycles is outlined in Scheme IV. The yields are lower (20–35%) than the expected statistical yield (50%) due to chromatographic losses. Combined low yields in this and the preceeding step limited the wall unit synthesis to the five indicated in Scheme IV. Reversible addition–elimination of the basic catalyst piperidine resulted in complete *cis* to *trans* isomerization of the unreacted olefin. A more hindered catalyst, 2,2,4,4-tetramethylpiperidine, preserved the *cis* stereochemistry of the starting diene. The olefin is ultimately lost, so the key issue here is formation of a single isomer, either *cis* or *trans*, to simplify increasingly complex ^{13}C NMR spectra. The dissymmetric case (**8TrgPOH**) forms with a modest regioselectivity favoring addition adjacent to the **Trg** side. Attempts to steer the reaction or to isolate a single isomer were fruitless: all regioisomers were carried forward as a mixture. Conversion to the mesylate (**YZPOMs**) and thence to the iodide (**YZPI**) proceeded smoothly, to complete the preparation of five potential wall components (**8$_2$PI**, **5$_2$PI**, **12$_2$PI**, **Trg$_2$PI**, and **8TrgPI**).

Linkage of the Wall Units to the Core. Numerous amide derivatives of crown ether carboxylic acids are known[17] but esters are rarely reported.[22] Our earlier report formed the core-to-wall ester linkage via the crown ether acid chloride.[11] Close inspection of the ^{13}C NMR signals for the crown ether methine carbons of several model esters formed from acid chlorides revealed additional complexities consistent with some loss of stereochemical integrity.[23] Since we were unable to reliably suppress this side reaction in model compounds, we turned to ester formation via carboxylate alkylation.

Using Cs_2CO_3 as the base[24] allowed the preparation of esters of the dicarboxylate crown ether **Di**, but gave no trace of any reaction with either the tetra- or hexaacids **Tet** and **Hex**.[23] The monocesium salt complexes of these two ligands crystallize readily from water and show well-

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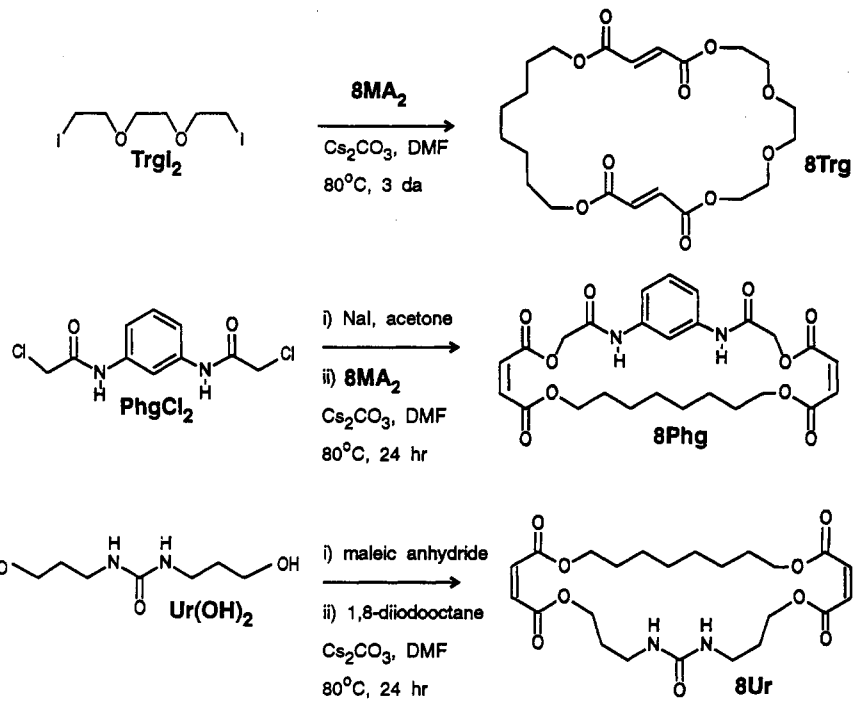
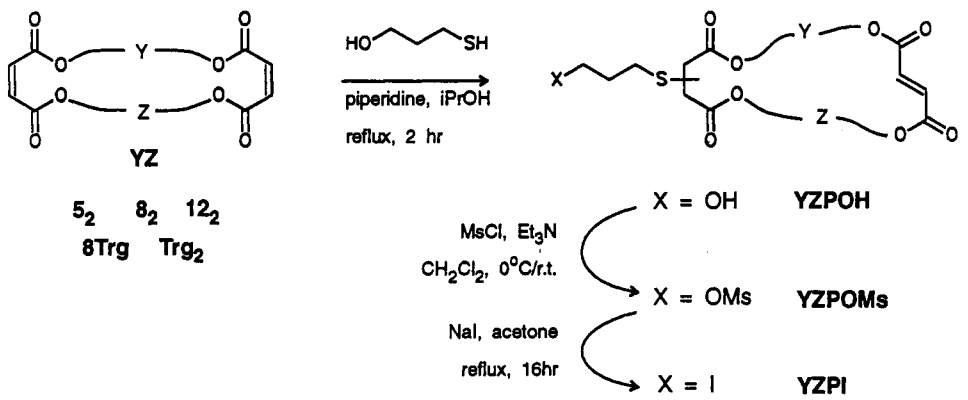
Scheme III



Scheme IV



organized Cs^+ binding sites in both cases.[25] Evidently this complex is quite unreactive since no esterification occurred, even under conditions where the reaction mixture was apparently homogeneous. The solution to this impasse was the use of a noncoordinating cation (Me_4N^+) as counterion to the crown ether carboxylate (Scheme V). Preparation of an anhydrous salt proved to be unreliable and we opted for use of stoichiometric tetramethylammonium pentahydrate to form the tetra- or hexakis salts. The water present provoked some competing hydrolysis of the wall unit iodide **YZPI** to give **YZPOH** in every case. Under the optimized conditions, a 2-fold excess of **YZPI** was used and the alcohols were recovered, for recycle, during the purification. Gel filtration with lipophilic Sephadex gave the products at the exclusion volume, well separated from low molecular weight byproducts. The isolated yields were typically 65–70% for derivatives of **Tet** and 50–55% for derivatives of **Hex**, corresponding to about 90% yield per ester formed.

Addition of Polar Head Groups. To complete the synthesis, two, four, or six head groups were added using the Michael addition of sulfur nucleophiles to the maleate units in the walls. Scheme V illustrates the complete synthesis of **(G8TrgP)$_6$Hex** as an example. Fuhrhop[18] previously had described a wide range of examples but we constrained our efforts to three simple cases: 1-thio-β-D-glucose,[20] 3-mercaptopropanol, and mercaptoacetate. A 2-fold excess of the small molecule reagent was used to drive the conversion to completion, as judged by the ^{13}C NMR spectra of crude product mixtures. Chromatographic losses of the final products were high in all cases due to the amphiphilic character of the materials, so the yields were typically 20–40% for this step. Addition of β-mercaptoethylamine as a potential head group resulted in aminolysis of the core-wall ester linkage in the three cases examined.

Figure 3 summarizes the 21 compounds prepared from the modular construction set and yield information expressed as overall efficiency for the two assembly steps per bond formed (4, 8, or 12). The average yield of isolated products for the ester formation step was 58%, but was only 22% for the Michael addition of head groups due to chromatographic losses. The average yield (isolated products) of the two steps was 13% (range 3–33%). On the basis of yield per bond formed, the esterification average efficiency is 83%, the head group addition average

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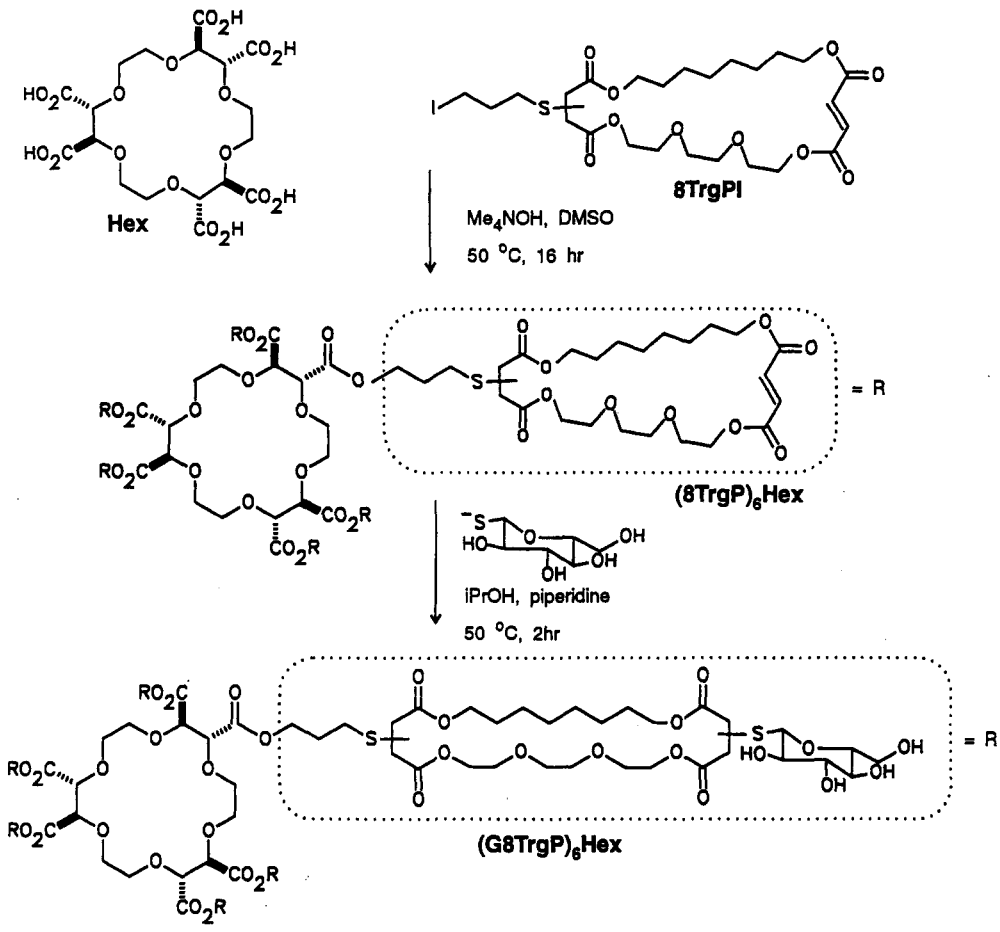
Scheme V



efficiency is 65%, and the overall average efficiency is 57% per wall unit/head group added. The main inefficiency in both steps is not the actual coupling reactions themselves, as NMR spectra of crude materials showed complete coupling had been achieved in all cases. Rather, the chromatographic losses, particularly of the amphiphilic final products, are the main source of inefficiency. Figure 3 shows the overall efficiency is higher for derivatives of **Tet** and **Hex**, than for derivatives of **Di**. The higher molecular weight materials are separated efficiently from low molecular weight byproducts during gel filtration, leading to better recoveries of purified products.

The suite offers a range of combinations for a structure–activity study and covers about 25% of the potential combinations of components of Figure 2. Despite the high average molecular weight (>2900 g/mol), the compounds behave as conventional organic materials. The compounds were prepared as mixtures of the regio- and stereoisomers, and no chromatographic fractionation of the mixtures was found in any case. Small regiochemical preferences were noted, but all of the expected regioisomeric lines were observed in the ^{13}C NMR. In homogeneous solution, independent molecular motions of the extremities of the molecules result in averaging of many of the potential diastereotopic signals. This fortunate occurance greatly simplified the complexity of the spectra, and in spite of the very large number of resonances all peaks could be assigned.[23] In the preliminary work, incomplete esterification was simple to detect by the additional multiplicity in the signals for the crown ether methine units. Incomplete Michael reaction for addition of head groups was simply detected in the olefin resonances.

Mass spectra of the products gave molecular ions in many cases. Two prominent fragmentation processes were diagnostic: a retro-Michael process to give the molecular ion minus a head group, $(M - head)^+$, and a cleavage in the propyl linkage β to the sulfur to result in $(M - wall)^+$. A retro-Michael reaction at the propylthio spacer would produce a daughter ion having the mass of a wall plus a head group. This ion was frequently the base peak. In many cases, fragments corresponding to sequential loss of one, two, and three wall units confirmed the structures assigned. Not surprisingly, the complexity of the mass spectra increased with the number of basic sites in the molecule. The least favorable cases involved the conjunction of the G head group and the $\mathbf{Trg_2}$ wall unit.

The modular or tinker-toy[19] approach to the construction of large structures imposes quite rigorous demands on the components and on the construction reactions. The components must have desired structural and functional characteristics, but must also be available in useful amounts. Some of our potential components fail in this regard (e.g. **8Ur** or **8Phg**). The efficiency of coupling reactions must be high, as ours are, but should ideally offer more regio-and stereochemical control than the processes used in this first-generation set. More structural control would be possible if the wall units were single isomers or achiral. Finally, structure without function is a sterile goal. Fortunately half of the materials prepared are active transporters and five can be shown to act by a channel mechanism consistent with the design proposal implied by Figure 1.[13]

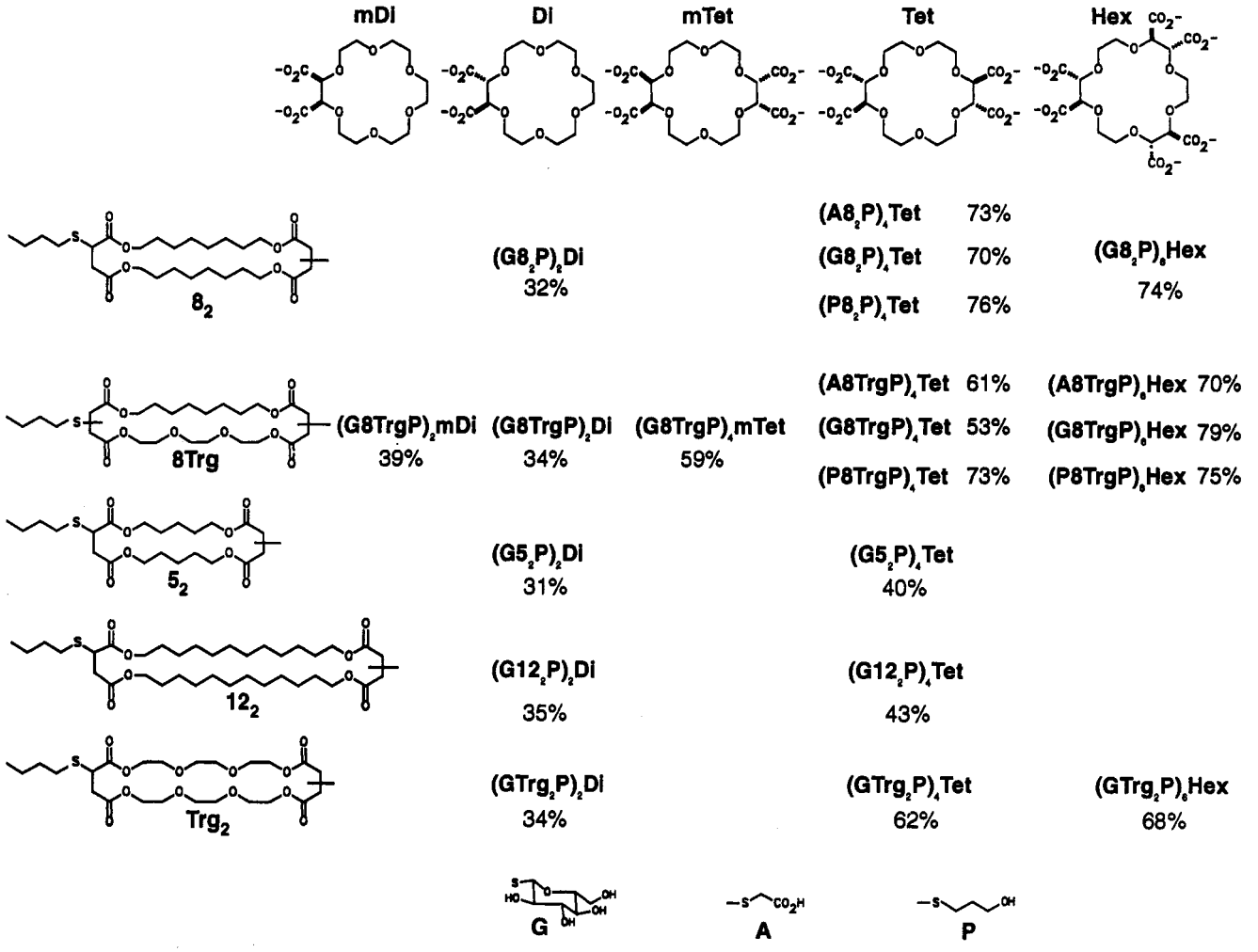


Figure 3. Compounds prepared and overall isolated yield per bond formed in the two coupling reactions.

Experimental Section

Melting points were taken on a Reichart hot-stage microscope (uncorrected). Proton NMR spectra were recorded with Perkin-Elmer R32 (90 MHz, CW), Bruker NM 250 (250 MHz, FT), or Bruker AMX 360 (360.14 MHz, FT) spectrometers in $CDCl_3$, CD_2Cl_2, or CD_3OD as solvent; 90-MHz ^1H NMR spectra (R32) were referenced to Me_4Si as internal standard, and all 360-MHz ^1H NMR spectra (AMX 360) were referenced with the central solvent line as standard (7.24 ppm for $CDCl_3$, 5.32 ppm for CD_2Cl_2, and 3.30 ppm for CD_3OD all relative to Me_4Si). Carbon spectra were recorded with either a Bruker WM 250 (62.89 MHz) or Bruker AMX 360 (90.57 MHz) with the central solvent line as standard (77.0 ppm for $CDCl_3$, 53.8 ppm for CD_2Cl_2, and 49.0 ppm for CD_3OD all relative to Me_4Si). Methane chemical ionization mass spectra were recorded on a Finnegan 3300 GC-MS instrument. LSIMS mass spectra were recorded with a Kratos Concept IH mass spectrometer using glycerol and/or thioglycerol as matrix. Elemental analyses were performed by Canadian Microanalytical Services, New Westminster, B.C.

The polycarboxylate crown ethers **Di** ((2*R*,3*R*)-1,4,7,10,13,-16-hexaoxacyclooctadecane-2,3-dicarboxylic acid), **mDi** ((2*R*,3*S*)-1,4,7,10,13,16-hexaoxacyclooctadecane-2,3-dicarboxylic acid), **Tet** ((2*R*,3*R*,11*R*,12*R*)-1,4,7,10,13,16-hexaoxacyclooctadecane-2,3,11,-12-tetracarboxylic acid), **mTet** ((2*R*,3*S*,11*R*,12*S*)-1,4,7,10,13,16-hexaoxacyclooctadecane-2,3,11,12-tetracarboxylic acid), and **Hex** ((2*R*,3*R*,8*R*,9*R*,14*R*,15*R*)-1,4,7,10,13,16-hexaoxacyclooctadecane-2,3,8,9,14,15-hexacarboxylic acid) were prepared as previously described.[14] The diene macrocycle $\mathbf{12_2}$ was prepared as described by Fuhrhop and had properties identical to those reported.[18] The iodide $\mathbf{TrgI_2}$ (1,2-bis(2-iodoethoxy)ethane) was prepared from the dichloride by halide exchange.[22]

General Procedure for Diacids. The diol (1 mol) and maleic anhydride (2 mol) were mixed in benzene (500 mL) and refluxed for 6 h. The benzene was removed under reduced pressure to give a solid product in quantitative yield that was used without further purification. The following diacids were prepared. $\mathbf{8MA_2}$ from 1,8-octanediol (146 g, 1 mol) and maleic anhydride (196 g, 2 mol): ^1H NMR 90 MHz (δ, $CDCl_3$) 9.8 (br s, 2H), 6.2 (s, 4H), 4.1 (t, J = 6Hz, 4H), 1.5 (m), 1.2 (br s); ^{13}C NMR, 62.89 MHz (δ, $CDCl_3$) 167.1, 166.5, 133.4, 130.5, 66.5, 28.8, 28.1, 25.5; MS (CI, *m/e*) 343 (M + 1). $\mathbf{5MA_2}$ from 1,5-pentanediol (104 g, 1 mol) and maleic anhydride (196 g, 2 mol, 2 equiv) mp 77–81 °C; ^1H NMR, 90 MHz (δ, $CDCl_3$) 6.3 (s, 4H), 4.2 (t, J = 6Hz, 8H), 1.6 (m, 6H); MS (CI, *m/e*) 301 (M + 1).

***N,N'*-Bis(3-hydroxypropyl)urea (Ur(OH)$_2$).** A mixture of diethyl carbonate (20.0 g, 169 mmol) and 3-amino-1-propanol (25.4 g, 338 mmol) was heated at 148–150 °C for 41 h. The crude product was recrystallized from acetonitrile (21.2 g, 71%): mp = 93–94 °C; ^1H NMR, 90 MHz (δ, D_2O) 3.5 (t, J = 7 Hz, 4H), 3.1 (t, J = 7 Hz, 4H), 1.6 (m, 4H); ^{13}C NMR, 62.89 MHz (δ, D_2O) 160.7, 59.2, 36.7, 31.8; MS (CI, *m/e*) 177 (M + 1). Anal. Calcd for $C_7H_{16}N_2O_3$: C, 47.71%; H, 9.15%; N, 15.9%. Found: C, 47.67%; H, 9.24%; N, 15.75%.

1,3-Bis(chloroacetamido)benzene (PhgCl$_2$). Chloroacetyl chloride (8.4 g, 74 mmol, 4 equiv) in dry THF (50 mL) was added dropwise into a solution of 1,3-phenylenediamine (2.0 g, 18 mmol) and triethylamine (12 mL, excess) in dry THF (50 mL) at room temperature under a N_2 atmosphere. The reaction was stirred for 48 h. The solvent was removed under reduced pressure and the black-colored residue was preadsorbed on a silica gel column. The product was eluted with dichloromethane/methanol (98:2). The solvent was evaporated under reduced pressure. The pale brown residue was taken up in 500 mL of dichloromethane which was washed with H_2O (400 mL) and saturated sodium bicarbonate solution (200 mL). The solution was dried over $MgSO_4$, filtered, and evaporated to dryness. The solid residue was recrystallized

from acetone and activated carbon to give **PhgCl$_2$** as a white solid (0.9 g, 18%): mp = 220–221 °C; ^{1}H NMR, 90 MHz (δ, CD_3COCD_3) 8.0 (br s, 2H), 7.2–7.5 (m, 4H), 4.2 (s, 4H); ^{13}C NMR 62.89 MHz (δ, CD_3COCD_3) 165.4, 139.9, 130.0, 116.2, 111.7, 44.1; MS (CI, *m/e*) 261 (M + 1). Anal. Calcd for $C_{10}H_{10}N_2Cl_2$: C, 46.00%; H, 3.86%; N, 10.73%; Cl, 27.16%. Found: C, 46.02%; H, 3.88%; N, 10.74%; Cl, 29.48%.

General Procedure for Diene Macrocycles YZ. The appropriate diacid (60 mmol) and diol (60 mmol) were dissolved in benzene (1.5 L). Methanesulfonic acid (1 mL) was added and the mixture was heated with azeotropic removal of water (Dean–Stark) for 12 h. The solvent was removed under reduced pressure to give a crude product. Purification details are given below.

8$_2$: The solid product from **8MA$_2$** (20.52 g, 60 mmol) and 1,8-octanediol (8.76 g, 60 mmol) was triturated with diethyl ether (200 mL) and then recrystallized from ethyl acetate, as a colorless crystalline solid (3.3 g, 7.3 mmol, 12%): mp 103–105 °C; ^{1}H NMR, 90 MHz (δ, $CDCl_3$) 6.2 (s, 4H), 4.2 (t, J = 6.2 Hz, 8H), 1.6 (m), 1.4 (br s); ^{13}C NMR, 100.12 MHz (δ, $CDCl_3$) 165.2, 129.6, 65.3, 29.1, 28.4, 25.8; MS (CI, *m/e*) 453 (M + 1), 481 (M + 29), 493 (M + 41). Anal. Calcd for $C_{24}H_{36}O_8$: C, 63.69%; H, 8.01%. Found: C, 63.60%; H, 7.96%.

8Trg: The oily products from three reactions of **8MA$_2$** (20.52 g, 60 mmol) and triethlene glycol (9.0 g, 60 mmol) were combined and preadsorbed onto alumina (250 g) and chromatographed on silica gel (450 g). Four fractions were obtained: 20% ethyl acetate/hexanes (6 L; **2** + **8$_2$**), 35% ethyl acetate/hexanes (4 L; **1** > **8Trg**), 50% ethyl acetate/hexanes (8 L; **1** < **8Trg**), and 100% ethyl acetate (4 L; **8Trg** + **Trg$_2$** + 1). The solvent was removed from fractions 2–4, and they were fractionated separately by Kugelrohr distillation. The first volatile fraction (10^{-3} mmHg, 120 °C) was **1** (clear oil); the second fraction (10^{-3} mmHg, 220 °C) was **8Trg**. Product-containing fractions were combined to give **8Trg** as a colorless solid (7 g, 15.3 mmol, 6.4%): ^{1}H NMR, 90 MHz (δ, $CDCl_3$) 6.2 (s, 4H), 4.2 (m, 8H), 3.7 (m, 4H), 3.6 (s, 4H), 1.6 (m), 1.4 (br s); ^{13}C NMR, 90.57 MHz (δ, $CDCl_3$) 165.1, 165.0, 130.2, 129.0, 70.5, 68.7, 65.2, 64.1, 28.7, 28.2, 25.5; MS (CI, *m/e*) 457 (M + 1). Anal. Calcd for $C_{22}H_{32}O_{10}$: C, 57.89%; H, 7.07%. Found: C, 58.14%; H, 7.10%.

Trg$_2$: Triethylene glycol (10 g, 67 mmol) and maleic anhydride (13.1 g, 134 mmol, 2 equiv) in benzene (1.5 L) were refluxed for 3 h. A further 10 g of triethylene glycol (67 mmol) and methanesulfonic acid (1 mL) were added, and the mixture was heated with azeotropic removal of water (Dean–Stark) for 12 h. The solvent was removed under reduced pressure and combined with two batches made analogously, and the oily products were preadsorbed from benzene onto alumina (200 g) and chromatographed on silica gel (250 g). Three fractions were collected: 50% ethyl acetate/hexanes (3 L), 60% ethyl acetate/hexanes (1 L), and 100% ethyl acetate (3 L, **Trg$_2$**). The solvent was removed from the third fraction and evacuated for 24 h (the procedure can be improved subsequently by seeding before evacuation). The solid was triturated with the minimum of ethyl acetate to afford a colorless solid (6.5 g, 15.2 mmol, 7.5%): ^{1}H NMR, 90 MHz (δ, $CDCl_3$) 6.2 (s, 4H), 4.2 (t, J = 3 Hz, 8H), 3.6 (m, 8H), 3.5 (s, 8H); ^{13}C NMR, 62.89 MHz (δ, $CDCl_3$) 165.0, 129.0, 70.5, 68.8, 64.3; MS (CI, *m/e*) 461 (M + 1), 489 (M + 29), 501 (M + 41). Anal. Calcd for $C_{20}H_{28}O_{12}$: C, 52.17%; H, 6.13%. Found: C, 51.9%; H, 6.03%.

5$_2$: The solid product from **5MA$_2$** (30 g, 0.1 mol) and 1,5-pentanediol (10.4 g, 0.1 mol) was triturated with diethyl ether (200 mL) and then recrystallized three times from ethyl acetate to afford a colorless crystalline solid (3.8 g, 10 mmol, 10%): mp 130–131 °C; ^{1}H NMR, 90 MHz ($CDCl_3$) 6.2 (s, 4H), 4.2 (t, J = 6 Hz, 8H), 1.8–1.3 (m, 12H); ^{13}C NMR, 62.89 MHz (δ, $CDCl_3$) 165.4, 129.8, 65.0, 28.1, 22.0; MS (CI, *m/e*) 369 (M + 1). Anal. Calcd for $C_{18}H_{24}O_8$: C, 58.69%; H, 6.57%. Found: C, 58.73%; H, 6.57%.

Ur$_2$: The diol **Ur(OH)$_2$** (2.0 g, 113 mmol), maleic anhydride (1.1 g, 113 mmol), and methanesulfonic acid (1 mL) was stirred at reflux in benzene (500 mL) with azeotropic removal of water (Dean–Stark) for 48 h (slow dissolution of solid diol). The solvent was evaporated under reduced pressure and the oily residue was purified by chromatography on silica gel (100 g). The product was eluted with dichloromethane/methanol (1:1), the solvent was removed, and the residue was dissolved in methanol (50 mL). Upon addition of diethyl ether (12 mL) to this solution, the product Ur$_2$ precipitated as a sticky oil (53 mg, 2%): ^{1}H NMR, 90 MHz (δ, CD_3OD) 6.2 (s, 4H), 4.2 (t, J = 7 Hz, 8H), 3.2 (t, J = 7 Hz, 8H), 1.7 (m, 8H); ^{13}C NMR 62.89 MHz (δ, CD_3OD) 167.2, 161.1, 131.1, 64.1, 37.8, 30.2; MS (CI, *m/e*) 513 (M + 1). Anal. Calcd for $C_{22}H_{32}N_4O_{10}$: C, 51.56%; H, 6.29%; N, 10.93%. Found: C, 51.32%; H, 6.22%; N, 10.18%.

8Trg by Carboxylate Alkylation. A mixture of the diacid **8MA$_2$** (6.8 g, 20 mmol) and the diiodide **TrgI$_2$** (7.4 g, 20 mmol) in dry DMF (200 mL) was added dropwise over a 54-h period into a stirred mixture of cesium carbonate (13.0 g, 40 mmol, 2 equiv) in dry DMF (200 mL) at 82 °C under a N_2 atmosphere. The reaction was heated for 67 h and the solvent was evaporated under reduced pressure. The solid residue was preadsorbed on neutral alumina (70 g) and chromatographed on a silica gel column. The product was eluted with hexane/ethyl acetate as a colorless oil (0.62 g, 7%). Spectral properties identical to those above except for the *trans* resonances in the NMR spectra: ^{1}H NMR δ 6.8 (s); ^{13}C NMR δ 133.5.

8Ur by Carboxylate Alkylation. A solution of the diol **Ur(OH)$_2$** (2.0 g, 11 mmol), maleic anhydride (2.23 g, 22 mmol, 2 equiv), and one drop of concd sulfuric acid in dry DMF (100 mL) was heated at 65 °C for 29 h. This solution was added to a dropping funnel containing 1,8-diiodooctane (4.15 g, 11 mmol) and dry DMF (150 mL) and the mixture was added dropwise over a 24-h period to a strirred suspension of cesium carbonate (7.50 g, 23 mmol, 2.1 equiv) in dry DMF (1.0 L) at 80 °C. The reaction was heated for a total of 39 h. The solvent was evaporated under reduced pressure, the residue was taken up in dichloromethane (600 mL) and was filtered, and the solvent was evaporated under reduced pressure. The product was purified on silica gel (120 g) eluted with dichloromethane/methanol (95:5). The solvent was evaporated to dryness and the pale yellow oily residue was triturated with diethyl ether (50 mL) to give **8Ur** as white crystalline needles (11 mg, 0.2%): mp = 133–134 °C; ^{1}H NMR, 90 MHz (δ, $CDCl_3$) 6.2 (s, 4H), 4.9 (br, 2H), 4.2 (m, 8H), 3.2 (t, J = 7 Hz, 4H), 1.9 (m, 4H), 1.6 (m, 4H), 1.4 (br s, 8H); ^{13}C NMR, 62.89 MHz (δ, $CDCl_3$) 165.7, 165.4, 158.2, 130.3, 129.2, 65.4, 63.0, 36.9, 28.8, 28.6, 28.2, 25.3; MS (CI, *m/e*) 483 (M + 1). Anal. Calcd for $C_{23}H_{34}N_2O_9$: C, 57.25%; H, 7.10%; N, 5.81%. Found: C, 57.22%; H, 6.94%; N, 5.73%.

8Phg: A mixture of the dichloride **PhgCl$_2$** (2.0 g, 7.6 mmol) and sodium iodide (11.5 g, 76 mmol, 10 equiv) in acetone (200 mL) was refluxed under a N_2 atmosphere for 20 h. The solvent was evaporated under reduced pressure. The crude diiodide was mixed with the diacid **8MA$_2$** (2.6 g, 7.6 mmol) in dry DMF (300 mL) and the mixture was added dropwise over a 12-h period to a stirred suspension of cesium carbonate (5.0 g, 15 mmol, 2 equiv) in dry DMF (200 mL) at 80 °C under a N_2 atmosphere. The reaction was heated for a total of 24 h. The solvent was removed under reduced pressure. The orange solid residue was taken up in chloroform (800 mL) and was washed with water (200 mL × 3). The organic layer was separated, dried over magnesium sulfate, and filtered, and the solvent was evaporated under reduced pressure. The residue was purified on a silica gel column (60 g) and the product was eluted with dichloromethane/methanol (98:2). Solvent was evaporated under reduced pressure and the residue was triturated with diethyl ether (300 mL) to give **8Phg** as a white powder (0.13 g, 3%): mp = 219–220 °C; ^{1}H NMR 90 MHz (δ, $CDCl_3$) 7.2–7.5 (m, 4H), 6.8 (s, 4H), 4.8 (s, 4H), 4.2 (t, J = 6 Hz, 4H), 1.6 (m, 4H), 1.4 (br, s, 8H); ^{13}C NMR, 62.89 MHz (δ, $CDCl_3$) 164.6, 164.5, 163.8, 137.3, 135.8, 131.5, 130.1, 116.8, 111.4, 65.5, 63.4, 28.9, 28.6, 25.7; MS (CI, *m/e*) 531 (M + 1). Anal. Calcd for $C_{26}H_{30}N_2O_{10}$: C, 58.86%; H, 5.70%; N, 5.28%. Found: C, 58.84%; H, 5.50%; N, 5.27%.

General Procedure for Wall Units: YZPOH, YZPOMs, YZPI. The macrocylic dienes (**YZ**) (25 mmol) and 3-mercapto-1-propanol (25 mmol) were dissolved in 2-propanol (200 mL) containing piperidine (1 mL) or 2,2,6,6-tetramethylpiperidine (0.5 mL), and the mixture was heated at reflux for 2 h (or 5 h at 60 °C for tetramethylpiperidine). The solvent was removed under reduced pressure and the product was chromatographed on 8% deactivated alumina (250 g) with a dichloromethane/hexane gradient (50:50 to 100% CH_2Cl_2). Unreacted macrocyclic diene was obtained in the early fractions eluted with 50%

dichloromethane; later fractions (50–100% CH_2Cl_2) contained the product. Combined product-containing fractions were evaporated to give **YZPOH**. The alcohols **YZPOH** (10 mmol) and triethylamine (50 mmol) were dissolved in dichloromethane (150 mL) and the mixture was cooled to −10 °C. Methanesulfonyl chloride (20 mmol) in dichloromethane (5 mL) was added dropwise over 30 min. The reaction was allowed to warm to room temperature and was stirred for a further 2 h. The reaction mixture was then washed with saturated sodium chloride (2 × 100 mL), 10% hydrochloric acid (2 × 100 mL), 10% sodium bicarbonate (2 × 100 mL), and again with saturated sodium chloride (2 × 100 mL), and dried over sodium sulfate, and the solvent was removed to give **YZPOMs**. The mesylates (6 mmol) and sodium iodide (48 mmol) were mixed in acetone (100 mL) and heated at reflux overnight. The solvent was removed under reduced pressure. The crude products were dissolved in dichloromethane (200 mL), washed with water (2 × 100 mL), and dried over sodium sulfate, and the solvent was removed under reduced pressure to give the iodides **YZPI**.

8_2POH. From 8_2 (12.5 g), using piperidine catalyst, as a clear oil (4.15 g, 76 mmol, 28%): ^{1}H NMR, 90 MHz (δ, $CDCl_3$) 6.8 (s, 2H), 4.2 (m, 8H), 3.7 (m, 3H), 3.2–2.7 (m, 4H), 2.4 (s, 1H), 2.0–1.2 (m, 26H); ^{13}C NMR, 62.89 MHz ($CDCl_3$) 171.7, 170.6, 165.0, 133.5, 65.3, 64.9, 61.1, 41.7, 36.6, 31.8, 28.4, 28.1, 26.0, 25.3; MS (CI, *m/e*) 545 (M + 1). Anal. Calcd for $C_{27}H_{44}O_9S$: C, 59.54%; H, 8.14%; S, 5.89%. Found: C, 59.65%; H, 8.01%; S, 5.52%.

8_2POMs. From **8_2POH** (4.15 g, 7.6 mmol) as a yellow oil (3.62 g, 5.8 mmol, 76%): ^{1}H NMR 90 MHz (δ, $CDCl_3$) 6.8 (s, 2H), 4.2 (m, 10H), 3.6 (dd, J = 3, 6 Hz, 1H), 2.9 (s, 3H), 3.1–2.6 (br m, 4H), 2.0 (m, 2H), 1.8–1.2 (br m, 24H); ^{13}C NMR, 62.89 MHz ($CDCl_3$) 171.2, 170.3, 164.8, 133.4, 67.8, 65.2, 64.8, 41.5, 37.2 36.4, 28.7, 28.6, 28.2, 25.9, 25.2, 21.3; MS (CI, *m/e*) 623 (M + 1).

8_2PI. From **8_2POMs** (3.62 g, 5.8 mmol), as a yellow oil (3.0 g, 46 mmol, 79%): ^{1}H NMR, 90 MHz (δ, $CDCl_3$) 6.8 (s, 2H), 4.2 (m, 8H), 3.65 (dd, J = 3, 6 Hz), 3.2 (t, J = 6 Hz), 3.0–2.7 (m, 4H), 2.1 (m, 2H), 1.8–1.3 (br m, 24H); ^{13}C NMR, 62.89 MHz ($CDCl_3$) 171.5, 170.4, 164.9, 133.5, 65.4, 64.9, 41.5, 36.6, 32.4, 32.0, 28.8, 28.4, 26.0, 25.3, 4.3; MS (CI, *m/e*) 655 (M + 1). Anal. Calcd for $C_{27}H_{43}O_8SI$: C, 49.54%; H, 6.62%; S, 4.90%; I, 19.39%. Found: C, 49.21%; H, 6.56%; S, 5.10%; I, 19.64%.

8TrgPOH. From 8Trg (5 g, 11 mmol), using piperidine as catalyst, as a clear oil (2.38 g, 4.3 mmol, 39%): ^{1}H NMR, 90 MHz (δ, $CDCl_3$) 6.8 (s, 2H), 4.2 (m, 8H), 3.6 (m, 11H), 3.0–2.6 (m, 4H), 1.8–1.1 (m, 15H); ^{13}C NMR, 62.89 MHz ($CDCl_3$) 171.6, 170.5, 164.9, 134.0, 133.1, 70.7, 70.6, 70.4, 69.2, 69.0, 68.9, 65.3, 65.2, 64.7, 64.5, 64.4, 64.2, 63.9, 60.9, 41.7, 41.5, 36.5, 36.4, 31.8, 31.7, 28.8, 28.6, 28.4, 28.3, 28.0, 25.6, 25.3; MS (CI, *m/e*) 549 (M + 1). Anal. Calcd for $C_{25}H_{40}O_{11}S$: C, 54.73%; H, 7.34%: S, 5.84%. Found: C, 54.88%; H, 7.49%; S, 5.64%.

8TrgPOMs. From **8Trg** (720 mg, 1.3 mmol), as a yellow oil (740 mg, 1.2 mmol, 90%): ^{1}H NMR, 90 MHz (δ, $CDCl_3$) 6.8 (s, 2H), 4.2 (m, 10H), 3.6 (m, 9H), 3.0 (s, 3H), 2.9–2.6 (m, 4H, 2.0 (m, 2H), 1.8–1.3 (m, 12H); ^{13}C NMR 62.89 MHz ($CDCl_3$) 171.3, 170.3, 164.9, 134.0, 133.1, 70.7, 70.6, 70.4, 69.2, 69.0, 67.8, 65.3, 64.8, 64.5, 64.3, 63.9, 41.6, 41.5, 37.3, 36.4, 36.3, 28.8, 28.5, 28.4, 28.3, 27.4, 25.6, 25.3.

8TrgPI. From **8TrgPOMs** (740 mg, 1.2 mmol), as a yellow oil (500 mg, 760 μmol, 63%): ^{1}H NMR, 90 MHz (δ, $CDCl_3$) 6.8 (s, 2H), 4.2 (m, 8H), 3.6 (m, 9H), 3.2 (t, J = 6 Hz), 2.9–2.6 (m, 4H), 2.0 (m, 2H), 1.7–1.2 (m, 12H); ^{13}C NMR, 62.89 MHz ($CDCl_3$) 171.3, 170.3, 164.8, 134.0, 133.0, 70.7, 70.6, 70.4, 69.1, 69.0, 65.3, 64.8, 64.5, 64.4, 64.3, 63.9, 41.5, 41.4, 36.4, 36.3, 32.3, 32.0, 31.9, 28.8, 28.6, 28.5, 28.3, 28.2, 25.6, 25.3, 4.4; MS (CI, *m/e*) 659 (M + 1). Anal. Calcd for $C_{25}H_{39}O_{10}SI$: C, 45.59%; H, 5.96%; S, 4.86%; I, 19.26%. Found: C, 45.72%; H, 5.91%; O, 4.71%; S, 19.04%.

Trg_2POH. From **Trg_2** (6.4 g, 14 mmol), using 2,2,6,6-tetramethylpiperidine catalyst in tetrahydrofuran solvent, as a clear oil (1.4 g, 2.5 mmol, 18%): ^{1}H NMR, 360 MHz (δ, $CDCl_3$) 6.2 (s, 2H), 4.3 (m, 8H), 3.7 (m, 19H), 2.9–2.6 (m, 4H), 2.0 (s, 1H), 1.8 (m, 2H); ^{13}C NMR, 62.89 MHz ($CDCl_3$) 171.4, 170.2, 165.0, 129.7, 70.5, 68.9, 68.8, 64.4, 64.3, 64.0, 61.0, 41.7, 36.4, 31.8, 28.1; MS (CI, *m/e*) 553 (M + 1). Anal. Calcd for $C_{23}H_{36}O_{13}S$: C, 49.99%; H, 6.57%; S, 5.80%. Found: C, 49.75%; H, 6.52%; S, 5.87%.

Trg_2POMs. From **Trg_2POH** (1.4 g, 2.5 mmol), as a yellow oil (1.23 g, 2.0 mmol, 80%): ^{1}H NMR, 360 MHz (δ, $CDCl_3$) 6.2 (s, 2H), 4.2 (m, 10H), 3.6 (m, 17H), 2.8–2.6 (m, 4H), 2.1 (m, 2H); ^{13}C NMR, 62.89 MHz ($CDCl_3$) 171.1, 170.0, 165.0, 129.7, 70.5, 68.7, 67.8, 64.5, 64.3, 64.0, 41.6, 37.3, 36.3, 32.0, 27.3.

Trg_2PI. From **Trg_2POMs** (1.23 g, 2.0 mmol), as a yellow oil (1 g, 1.5 mmol, 75%): ^{1}H NMR, 360 MHz (δ, $CDCl_3$) 6.2 (s, 2H), 4.2 (m, 8H), 3.6 (m, 17H), 3.2 (t, J = 6 Hz, 2H), 3.0–2.6 (m, 4H), 2.0 (m, 2H); ^{13}C NMR, 62.89 MHz ($CDCl_3$) 171.1, 170.0, 165.0, 129.7, 70.6, 68.9, 68.8, 64.5, 64.3, 64.0, 41.6, 36.4, 32.0, 32.3, 4.5; MS (CI, *m/e*) 663 (M + 1). Anal. Calcd for $C_{23}H_{35}O_{12}SI$: C, 41.70%; H, 5.33%; S, 4.84%. Found: C, 42.36%; H, 5.03%; S, 5.16%.

5_2POH. From 5_2 (5 g, 14 mmol), using piperidine catalyst, as a clear oil (960 mg, 2.0 mmol, 14%): ^{1}H NMR, 360 MHz (δ, $CDCl_3$) 6.8 (s, 2H), 4.2 (m, 8H), 3.7 (m, 3H), 2.9–2.6 (m, 4H), 2.0 (s, 1H), 1.8 (m, 2H), 1.7–1.5 (m, 12H); ^{13}C NMR, 90.57 MHz ($CDCl_3$) 171.3, 170.3, 165.0, 164.9, 133.4, 65.0, 64.9, 64.6, 60.6, 42.5, 36.0, 31.4, 28.4, 28.3, 27.9, 23.2, 22.9; MS (CI, *m/e*) 461 (M + 1). Anal. Calcd for $C_{21}H_{32}O_9S$: C, 54.77%; H, 7.00%; S, 6.96%. Found: C, 54.83%; H, 6.94%; S, 7.35%.

5_2POMs. From **5_2POH** (960 mg, 2 mmol), as a yellow oil (900 mg, 1.7 mmol, 85%): ^{1}H NMR, 360 MHz (δ, $CDCl_3$) 6.8 (s, 2H), 4.2 (m, 10H), 3.6 (dd, J = 3, 6 Hz, 1H), 2.9–2.6 (m, 4H), 2.0 (m, 2H), 1.8–1.4 (m, 12H); ^{13}C NMR, 90.57 MHz ($CDCl_3$) 170.9, 169.9, 164.6, 133.2, 67.6, 64.8, 64.7, 64.3, 42.2, 37.1, 35.7, 28.2, 28.1, 27.9, 27.2, 22.9, 22.8.

5_2PI. From **5_2POMs** (900 mg, 1.7 mmol), as a yellow oil (540 mg, 940 μmol, 55%): ^{1}H NMR, 360 MHz (δ, $CDCl_3$) 6.7 (s, 2H), 4.1 (m, 8H), 3.5 (dd, J = 3, 6 Hz, 1H), 3.1 (t, 2H), 2.8–2.5 (m, 4H), 1.9 (m, 2H), 1.7–1.4 (m, 12H); ^{13}C NMR, 90.57 MHz ($CDCl_3$) 170.8, 169.8, 164.6, 133.2, 64.8, 64.7, 64.3, 42.1, 35.8, 31.8, 31.7, 28.2, 28.0, 22.9, 22.8, 4.5; MS (CI, *m/e*) 571 (M + 1). Anal. Calcd for $C_{21}H_{31}O_8SI$: C, 44.22%; H, 5.48%; S, 5.62%; I, 22.25%. Found: C, 44.21%; H, 5.45%; S, 6.13%; I, 21.89%.

12_2POH. I 12_2 (5.5 g, 9.8 mmol), using piperidine catalyst, as a colorless solid (720 mg, 1.1 mmol, 11%): ^{1}H NMR 360 MHz (δ, $CDCl_3$) 6.8 (s, 2H), 4.2 (m, 8H), 3.7 (m, 3H), 3.0–2.6 (m, 4H), 1.8 (m, 2H), 1.5–1.2 (m, 41H); ^{13}C NMR, 62.89 MHz ($CDCl_3$) 171.3, 170.4, 165.0, 133.6, 65.4, 65.1, 61.1, 41.8, 36.6, 31.7, 29.2, 29.0, 28.4, 28.0, 25.9, 25.6; MS (CI, *m/e*) 657 (M + 1). Anal. Calcd for $C_{35}H_{59}O_9S$: C, 64.09%; H, 9.06%; S, 4.88%. Found: C, 64.23%; H, 9.08%; S, 5.26%.

12_2POMs. From **12_2POH** (720 mg, 1.1 mmol), as a pale yellow semisolid (740 mg, 1.0 mmol, 90%): ^{1}H NMR, 360 MHz (δ, $CDCl_3$) 6.8 (s, 2H), 4.2 (m, 8H), 3.6 (dd, J = 3, 6 Hz), 3.0 (s, 3H), 3.2–2.6 (m, 4H), 2.0 (m, 2H), 1.7–1.1 (m, 40H); ^{13}C NMR, 62.89 MHz ($CDCl_3$) 171.3, 170.4, 165.0, 133.5, 67.8, 65.6, 65.4, 65.1, 41.7, 37.4, 36.5, 29.2, 29.0, 28.4, 28.4, 27.4, 25.9, 25.6.

12_2PI. From **12_2POMs** (740 mg, 1.0 mmol), as a yellow semisolid (640 mg, 830 μmol, 83%): ^{1}H NMR 360 MHz (δ, $CDCl_3$) 6.8 (s, 2H), 4.2 (m, 8H), 3.6 (dd J = 3, 6 Hz, 1H), 3.2 (t, 2H), 3.0–2.5 (m, 4H), 2.1 (m, 2H), 1.7–1.1 (m, 40H); ^{13}C NMR, 62.89 MHz ($CDCl_3$) 171.3, 170.4, 165.0, 133.5, 65.6, 65.4, 65.1, 41.6, 36.6, 32.4, 32.0, 29.3, 29.0, 28.5, 25.9, 25.6, 4.4; MS (CI, *m/e*) 767 (M + 1). Anal. Calcd for $C_{35}H_{58}O_8SI$: C, 54.89%; H, 7.63%; S, 4.18%; I, 16.55%. Found: C, 54.98%; H, 7.88%; S, 4.76; I, 16.88%.

General Procedure for Linkage of Wall Units to Core Units. To a stirred solution of the appropriate crown ether carboxylic acid (**Core**) (500 μmol) in methyl sulfoxide (20 mL) at 60 °C under argon, was added tetramethylammonium hydroxide (1 equiv per CO_2H). To this solution, the iodide **YZPI** (1.1–2 equiv per CO_2H as noted below) was added as a solution in methyl sulfoxide (2 mL), and the mixture was stirred for a further 4 h. The resulting amber solution was evaporated to dryness, dissolved in 4:3 chloroform/methanol (2 mL), filtered, and chromatographed on a gel filtration column (Sephadex LH-20, 4 × 20 cm). The product was collected in 1-mL fractions near the void volume. Later fractions contained **YZPOH** from hydrolysis. The product-containing fractions were identified by TLC on silanized silica (Merck RP-2, 5% CH_3OH in $CHCl_3$, I_2 stain) and were combined to yield the product **(YZP)$_x$Core.**

(8_2P)$_2$Di. From **Di** (138 mg, 390 μmol) and **8_2PI** (1 g, 1.53 mmol) as a yellow oil (200 mg, 141 μmol, 36%): ^{1}H NMR, 360 MHz (δ, $CDCl_3$) 6.8 (s, 4H), 4.4 (s, 2H), 4.2–4.0 (m, 20H), 3.7 (m, 2H), 3.6 (br m, 20H), 3.0–2.5 (m, 8H), 1.9 (m, 4H), 1.5–1.2 (m,

48H); ^{13}C NMR, 90.57 MHz ($CDCl_3$) 171.4, 170.4, 164.8, 169.2, 133.4, 79.6, 71.0, 70.6, 70.4, 70.3, 65.2, 64.8, 63.4, 41.4, 36.4, 28.8, 28.7, 28.4, 28.3, 25.9, 25.2, 28.1, 27.8. Anal. Calcd for $C_{68}H_{108}O_{28}S_2$: C, 58.10%; H, 7.74%; S, 4.56%. Found: C, 57.84%; H, 7.52%; S, 4.97%.

(8_2P)$_4$Tet. From **Tet** (48 mg, 110 μmol) and **8_2PI** (600 mg, 917 μmol), as a yellow oil (205 mg, 78 μmol, 71%): ^{1}H NMR, 360 MHz (δ, CD_2Cl_2): 6.8 (s, 8H), 4.3 (s, 4H), 4.2–4.0 (m, 40H), 3.8 (m, 4H), 3.6 (br m, 16H), 3.0–2.6 (m, 16H), 2.0 (m, 8H), 1.6–1.2 (br m, 96H); ^{13}C NMR, 90.57 MHz (CD_2Cl_2) 171.7, 170.8, 165.2, 169.5, 133.8, 80.3, 71.5, 70.5, 65.6, 65.5, 65.3, 65.2, 63.9, 41.9, 36.9, 29.8, 29.2, 28.8, 28.7, 28.7, 28.6, 28.2, 26.4, 25.7, 25.6. Anal. Calcd for $C_{124}H_{192}O_{48}S_4$: C, 58.47; H, 7.59; S, 5.03. Found: C, 58.05; H, 7.49; S, 5.32.

(8_2P)$_6$Hex. From **Hex** (40 mg, 76 μmol) and **8_2PI** (603 mg, 920 μmol), as a yellow oil (151 mg, 41 μmol, 53%): ^{1}H NMR, 360 MHz (δ, CD_2Cl_2) 6.8 (s, 12H), 4.4 (s, 6H), 4.3–3.9 (m, 60H), 3.7 (m, 6H), 3.6 (br s, 12H), 3.0–2.5 (m, 24H), 1.9 (m, 12H), 1.7–1.1 (br m, 144H); ^{13}C NMR, 90.57 MHz (CD_2Cl_2) 171.7, 170.8, 165.2, 169.4, 133.7, 80.2, 70.9, 65.6, 65.5, 65.1, 63.9, 41.8, 36.9, 29.3, 29.3, 29.2, 28.7, 28.6, 28.2, 26.4, 25.7, 25.6. Anal. Calcd for $C_{180}H_{276}O_{66}S_6$: C, 58.61%; H, 7.54%; S, 5.22%. Found: C, 58.45%; H, 7.38%; S, 5.80%.

(8TrgP)$_2$Di. From **Di** (67 mg, 190 μmol) and **8TrgPI** (500 mg, 760 μmol), as a yellow oil (180 mg, 128 μmol, 67%): ^{1}H NMR, 360 MHz (δ, $CDCl_3$) 6.8 (s, 4H), 4.3 (s, 2H), 4.2–3.9 (m, 20H), 3.8 (m, 2H), 3.6 (br m, 36H), 3.0–2.5 (m, 8H), 1.9 (m, 4H), 1.7–1.2 (br m, 24H); ^{13}C NMR, 90.57 MHz ($CDCl_3$) 171.3, 170.4, 170.3, 164.8, 164.7, 169.3, 134.0, 133.1, 79.6, 71.0, 70.8, 70.7, 70.6, 70.4, 70.3, 69.0, 68.9, 65.3, 65.2, 64.8, 64.4, 64.3, 64.2, 63.8, 63.4, 41.5, 41.4, 36.5, 36.3, 28.7, 28.6, 28.4, 28.3, 28.1, 27.9, 27.8, 25.8, 25.7, 25.3, 25.2. Anal. Calcd for $C_{84}H_{100}O_{30}S_2$: C, 54.38%; H, 7.13%; S, 4.54%. Found: C, 53.94%; H, 7.13%; S, 4.43%.

(8TrgP)$_2$mDi. From **mDi** (67 mg, 190 μmol) and **8TrgPI** (500 mg, 760 μmol), as a yellow oil (170 mg, 120 μmol, 63%): ^{1}H NMR, 360 MHz (δ, $CDCl_3$): 6.8 (s, 4H), 4.6 (s, 2H), 4.3–3.9 (m, 20H), 3.8 (m, 2H), 3.6 (br m, 36H), 3.0–2.5 (m, 8H), 1.9 (m, 4H), 1.7–1.1 (br m, 24H); ^{13}C NMR, 90.57 MHz ($CDCl_3$) 171.2, 171.1, 170.2, 170.1, 164.6, 164.5, 169.0, 133.7, 132.8, 80.2, 70.7, 70.6, 70.5, 70.4, 70.3, 70.2, 68.7, 65.0, 64.9, 64.5, 65.2, 64.1, 64.0, 63.6, 63.2, 41.3, 41.1, 36.3, 36.1, 28.5, 28.4, 28.3, 28.1, 28.0, 27.7, 27.5, 25.5, 25.4, 25.0, 24.9. Anal. Calcd for $C_{84}H_{100}O_{30}S_2$: C, 54.38%; H, 7.13%; S, 4.54%. Found: C, 53.86%; H, 6.78%; S, 4.83%.

(8TrgP)$_4$Tet. From **Tet** (83.6 mg, 190 μmol) and **8TrgPI** (1 g, 1.52 mmol), as a yellow oil (320 mg, 125 μmol, 66%): ^{1}H NMR, 360 MHz (δ, $CDCl_3$): 6.8 (s, 8H), 4.4–4.0 (br m, 44H), 3.7–3.5 (br m, 52H), 3.0–2.5 (m, 16H), 1.9 (m, 8H), 1.7–1.2 (br m, 48H); ^{13}C NMR, 90.57 MHz (CD_2Cl_2) 171.8, 171.6, 170.8, 170.6, 165.2, 165.1, 169.5, 134.3, 133.3, 80.1, 71.0, 70.8, 69.3, 71.5, 70.5, 65.6, 65.5, 64.9, 64.8, 64.3, 64.0, 42.0, 41.8, 36.9, 36.7, 29.2, 29.1, 29.0, 28.9, 28.8, 28.7, 28.6, 28.5, 28.3, 26.1, 25.7, 25.6. Anal. Calcd for $C_{116}H_{176}O_{54}S_4$: C, 54.36%; H, 6.92%; S, 5.05%. Found: C, 54.07%; H, 6.84%; S, 5.45%.

(8TrgP)$_4$mTet. From **mTet** (42 mg, 95 μmol) and **8TrgPI** (500 mg, 760 μmol), as a yellow oil (160 mg, 62 μmol, 65%): ^{1}H NMR, 360 MHz (δ, $CDCl_3$) 6.8 (s, 8H), 4.5 (s, 4H), 4.3–4.0 (br m, 40H), 3.7–3.5 (br m, 52H), 3.0–2.5 (m, 16H), 1.9 (m, 8H), 1.7–1.2 (br m, 48H); ^{13}C NMR, 90.57 MHz ($CDCl_3$) 171.3, 170.4, 164.8, 168.9, 134.0, 133.1, 80.3, 80.0, 72.5, 70.8, 70.7, 70.4, 70.3, 68.9, 65.3, 65.2, 64.8, 64.4, 64.3, 63.9, 63.6, 63.5, 41.5, 41.4, 36.5, 36.4, 28.7, 28.6, 28.4, 28.3, 28.2, 27.9, 27.8, 25.7, 25.3, 25.2. Anal. Calcd for $C_{116}H_{176}O_{54}S_4$: C, 54.36%; H, 6.92%; S, 5.00%. Found: C, 54.15%; H, 7.00%; S, 5.36%.

(8TrgP)$_6$Hex. From **Hex** (66 mg, 125 μmol) and **8TrgPI** (1 g, 1.52 mmol), as a yellow oil (151 mg, 41 μmol, 53%): ^{1}H NMR, 360 MHz (δ, CD_2Cl_2) 6.8 (s, 12H), 4.4–4.0 (br m, 66H), 3.7–3.5 (br m, 66H), 3.0–2.5 (m, 24H), 1.9 (m, 12H), 1.7–1.2 (br m, 72H); ^{13}C NMR, 90.57 MHz (CD_2Cl_2) 171.6, 170.8, 165.2, 165.1, 169.4, 134.3, 133.3, 80.2, 71.1, 71.0, 70.8, 69.3, 69.2, 65.6, 65.5, 65.1, 64.9, 64.8, 63.9, 42.0, 41.7, 36.9, 36.7, 29.2, 29.0, 28.9, 28.7, 28.6, 28.5, 28.3, 28.0, 26.2, 25.8, 25.6. Anal. Calcd for $C_{168}H_{252}O_{78}S_6$: C, 54.36%; H, 6.84%; S, 5.18%. Found: C, 54.20%; H, 6.70%; S, 5.53%.

(Trg$_2$P)$_2$Di. From **Di** (73.5 mg, 209 μmol) and **Trg$_2$PI** (320 mg, 483 μmol), as a yellow oil (140 mg, 98 μmol, 47%): ^{1}H NMR, 360 MHz (δ, $CDCl_3$) 6.2 (s, 4H), 4.4 (s, 2H), 4.3–4.0 (m, 20H), 3.8 (m, 2H), 3.7–3.6 (br m, 52H), 3.0–2.6 (m, 8H), 1.9 (m, 4H); ^{13}C NMR, 62.89 MHz ($CDCl_3$) 171.1, 170.1, 165.0, 169.3, 129.7, 129.6, 79.7, 71.0, 70.5, 70.3, 68.8, 68.7, 64.6, 64.5, 64.2, 63.4, 41.7, 36.4, 28.1, 27.9. Anal. Calcd for $C_{80}H_{92}O_{34}S_2$: C, 50.7%; H, 6.52%; S, 4.51%. Found: C, 50.00%; H, 6.43%; S, 5.02%.

(Trg$_2$P)$_4$Tet. From **Tet** (29 mg, 66 μmol) and **Trg$_2$PI** (200 mg, 302 μmmol), as a yellow oil (95 mg, 37 μmol, 56%): ^{1}H NMR, 360 MHz (δ, CD_2Cl_2) 6.3 (s, 8H), 4.4–4.1 (m, 44H), 3.8 (m, 4H), 3.7–3.5 (br m, 80H), 3.0–2.6 (m, 16H), 2.0 (m, 8H); ^{13}C NMR, 90.57 M Hz (CD_2Cl_2) 171.5, 170.5, 165.4, 169.5, 130.1, 130.0, 80.3, 70.9, 69.2, 69.1, 69.0, 71.5, 70.4, 65.2, 64.9, 64.8, 64.4, 63.9, 42.0, 36.8, 28.5, 28.2. Anal. Calcd for $C_{108}H_{160}O_{62}S_4$: C, 50.30%; H, 6.25%; S, 4.97%. Found: C, 50.21%; H, 6.34%; S, 5.12%.

(Trg$_2$P)$_6$Hex. From **Hex** (22.9 mg, 43 μmol) and **Trg$_2$PI** (200 mg, 302 μmol), as a yellow oil (80 mg, 21 μmol, 49%): ^{1}H NMR, 360 MHz (δ, CD_2Cl_2) 6.3 (s, 12H), 4.5–4.1 (m, 66H), 3.8–3.5 (br m, 114H), 3.0–2.5 (m, 24H), 1.9 (m, 12H); ^{13}C NMR, 90.57 MHz (CD_2Cl_2) 171.5, 170.5, 165.5, 165.4, 169.4, 130.2, 130.0, 80.3, 70.9, 69.2, 69.1, 64.9, 64.8, 64.5, 64.2, 63.9, 42.0, 36.8, 28.5, 28.3. Anal. Calcd for $C_{156}H_{228}O_{90}S_6$: C, 50.15%; H, 6.15%. Found: C, 50.58%; H, 6.50%.

(5_2P)$_2$Di. From **Di** (40 mg, 114 μmol) and **5_2PI** (180 mg, 416 μmol), as a yellow oil (80 mg, 64 μmol, 56%): ^{1}H NMR, 360 MHz (δ, $CDCl_3$) 6.8 (s, 4H), 4.4 (s, 2H), 4.1 (m, 20H), 3.8 (m, 2H), 3.6 (m, 20H), 2.9–2.5 (m, 8H), 1.9 (m, 4H), 1.8–1.4 (br m, 24H); ^{13}C NMR, 90.57 MHz ($CDCl_3$) 171.0, 170.0, 164.8, 164.7, 169.2, 133.4, 133.3, 79.6, 71.1, 70.6, 70.5, 70.3, 64.9, 64.5, 63.4, 42.4, 35.9, 28.4, 28.3, 28.2, 28.1, 28.0, 27.0, 23.0. Anal. Calcd for $C_{56}H_{84}O_{26}S_2$: C, 54.36%; H, 6.84%; S, 5.18%. Found: C, 53.94%; H, 6.83%; S, 5.54%.

(5_2P)$_4$Tet. From **Tet** (37 mg, 84 μmol) and **5_2PI** (250 mg, 439 μmmol), as a yellow oil (120 mg, 54 μmol, 64%): ^{1}H NMR 360 MHz (δ, $CDCl_3$) 6.8 (s, 8H), 4.4–4.0 (m, 44H), 3.8 (m, 4H), 3.7–3.5 (m, 16H), 2.9–2.5 (m, 16H), 1.9 (m, 8H), 1.8–1.5 (br m, 48H); ^{13}C NMR, 62.89 MHz ($CDCl_3$) 171.2, 170.2, 165.9, 169.3, 133.6, 133.5, 80.1, 71.8, 70.4, 65.1, 64.7, 63.6, 42.6, 36.2, 28.6, 28.5, 28.3, 28.2, 23.3, 23.2. Anal. Calcd for $C_{100}H_{144}O_{46}S_4$: C, 54.33%; H, 6.56%; S, 5.80%. Found: C, 54.05%; H, 6.56%; S, 6.09%.

(12$_2$P)$_2$Di. From **Di** (35 mg, 99 μmol) and **12$_2$PI** (230 mg, 300 μmol), as a yellow oil (100 mg, 61 μmol, 62%): ^{1}H NMR, 360 MHz (δ, $CDCl_3$) 6.8 (s, 4H), 4.4 (s, 2H), 4.2–3.9 (m, 20H), 3.8 (m, 2H), 3.6 (m, 20H), 3.0–2.5 (m, 8H), 1.9 (m, 4H), 1.7–1.1 (br m, 80H); ^{13}C NMR, 90.57 MHz ($CDCl_3$) 171.7, 170.7, 165.3, 169.7, 133.8, 80.0, 71.1, 70.8, 70.7, 70.6, 65.7, 65.4, 63.9, 42.0, 36.9, 29.8, 29.7, 29.5, 28.9, 28.8, 28.6, 28.3, 26.4, 26.1, 26.0. Anal. Calcd for $C_{84}H_{140}O_{26}S_2$: C, 61.89%; H, 8.66%; S, 3.93%. Found: C, 61.61%; H, 8.63%; S, 3.84%.

(12$_2$P)$_4$Tet. From **Tet** (30 mg, 68 μmol) and **12$_2$PI** (286 mg, 373 μmmol), as a yellow oil (105 mg, 35 μmol, 51%): ^{1}H NMR, 360 MHz (δ, $CDCl_3$) 6.8 (s, 8H), 4.3 (s, 4H), 4.2–3.9 (m, 40H), 3.8–3.4 (m, 20H), 3.0–2.5 (m, 16H), 1.9 (m, 8H), 1.8–1.5 (br m, 160H); ^{13}C NMR, 90.57 MHz ($CDCl_3$) 171.3, 170.4, 165.0, 169.3, 133.5, 80.0, 71.6, 70.4, 65.4, 65.1, 63.5, 41.6, 36.5 , 29.3, 29.0, 28.4, 28.2, 27.9, 26.0, 25.6. Anal. Calcd for $C_{156}H_{256}O_{46}S_4$: C, 62.54%; H, 8.61%; S, 4.28%. Found: C, 62.52%; H, 8.73%.

General Procedure for the Addition of Thioglucose Head Group (G). To a stirred solution of **(YZP)$_x$Core** (50 μmol) in 50:50 2-propanol/tetrahydofuran (20 mL), at 50 °C under nitrogen, methanesulfonic acid (19 mg, 200 μmol) as a 2-propanol solution was added. To this solution was added 1-thio-β-D-glucose sodium salt dihydrate (2 equiv per alkene), followed by 2,2,6,6-tetramethylpiperidine (0.25 mL) to adjust the pH to 8, and the cloudy solution was stirred a further 12 h at 50 °C. The solvent was removed under reduced pressure, and the product was dissolved in 4:3 chloroform/methanol (2 mL), filtered, and chromatographed by gel filtration (Sephadex LH-20, 4 × 20 cm). The product was collected in 1-mL fractions near the void volume. The product-containing fractions were identified by TLC (silanized silica, Merck RP-2, 5% CH_3OH in $CHCl_3$ eluent, I_2 stain) and combined, and the solvent was removed to give **(GYZP)$_x$Core**. The ^{1}H NMR spectra of the products were recorded, but due to the large number of exchangeable protons were relatively uniformative. All spectra were consistent with complete Michael addition as evidenced by the lack of olefinic resonances. General features (δ, $CDCl_3$): 4.4–4.0, 3.7–3.5, 3.0–2.5, 2.0–1.8, 1.7–1.1.

(G8_2P)$_2$Di. From **(8_2P)$_2$Di** (68.9 mg, 48.6 μmol) as a clear oil (24.4 mg, 13.6 μmol, 28%): ^{13}C NMR, 90.57 MHz (CD_3OD) 173.5,

173.3, 173.0, 172.2, 172.1, 171.9, 171.3, 86.4, 85.8, 82.1, 82.0, 80.3, 79.6, 79.5, 71.5, 70.9, 66.7, 66.5, 66.0, 65.3, 62.8, 42.9, 42.8, 41.2, 38.8, 37.9, 37.7, 30.3, 29.7, 29.5, 29.0, 26.9; MS (LSIMS, glycerol) 1798 (M + 1), 1101 (M – wall).

(G8$_2$P)$_4$Tet. From **(8$_2$P)$_4$Tet** (65.0 mg, 25.4 μmol), as a clear oil (28.5 mg, 8.5 μmol, 33%): ^{13}C NMR 90.57 MHz (CD_3OD) 173.4, 173.3, 172.9, 172.2, 172.0, 171.9, 171.0, 86.4, 85.5, 82.0, 81.9, 80.0, 74.3, 71.7, 71.7, 71.6, 71.2, 70.9, 66.8, 66.5, 66.1, 65.3, 62.9, 43.0, 42.8, 41.2, 38.8, 38.0, 37.8, 30.4, 29.8, 29.0, 27.0; MS (LSIMS, glycerol) 3354 (M + Na), 3136 (M – head), 2634 (M – wall).

(G8$_2$P)$_6$Hex. From **(8$_2$P)$_6$Hex** (64.0 mg, 17.6 μmol), as a clear oil (25.9 mg, 5.3 μmol, 31%): ^{13}C NMR, 90.57 MHz (CD_3OD) 173.4, 173.3, 172.8, 172.2, 172.1, 171.9, 170.8, 86.5, 85.8, 82.1, 82.0, 80.6, 79.6, 79.5, 74.3, 71.3, 71.2, 66.8, 66.6, 66.1, 65.6, 62.9, 43.0, 42.8, 41.2, 38.0, 37.8, 30.4, 29.8, 29.5, 29.4, 29.1, 26.9; MS (LSIMS, thioglycerol) 4887 (M + Na), 4669 (M – head), 4167 (M – wall).

(G8TrgP)$_2$Di. From **(8TrgP)$_2$Di** (69.0 mg, 49.0 μmol), as a clear oil (14.6 mg, 8.1 μmol, 17%): ^{13}C NMR, 90.57 MHz (CD_3OD) 173.4, 173.3, 173.0, 172.2, 172.0, 171.3, 86.4, 85.8, 80.4, 79.6, 79.5, 74.3, 71.6, 71.3, 70.9, 70.0, 66.7, 66.4, 65.9, 65.7, 65.1, 62.8, 42.9, 42.7, 41.2, 37.8, 37.6, 37.5, 30.1, 29.5, 28.9, 26.8, 26.6; MS (LSIMS, glycerol) 1805 (M + 1), 1104 (M – wall).

(G8TrgP)$_2$mDi. From **(8TrgP)$_2$mDi** (60.0 mg, 42.6 μmol), as a clear oil (18.8 mg, 10.4 μmol, 24%): ^{13}C NMR, 90.57 MHz (CD_3OD) 173.5, 173.3, 173.1, 172.2, 172.1, 171.0, 86.5, 85.8, 81.9, 81.8, 81.6, 79.6, 79.5, 74.3, 71.9, 71.8, 71.6, 71.5, 71.3, 71.2, 70.0, 66.7, 66.4, 66.0, 65.8, 65.2, 64.8, 62.9, 43.0, 42.8, 41.2, 38.6, 37.7, 37.6, 30.1, 29.9, 29.6, 29.0, 26.7; MS (LSIMS, glycerol) 1805 (M + H), 1827 (M + Na), 1104 (M – wall).

(G8TrgP)$_4$Tet. From **(8TrgP)$_4$Tet** (70.0 mg, 27.3 μmol), as a clear oil (11.2 mg, 3.3 μmol, 12%): ^{13}C NMR, 90.57 MHz (CD_3OD) 173.5, 173.4, 173.0, 172.2, 172.0, 171.1, 86.5, 85.8, 82.0, 79.8, 79.6, 79.4, 74.3, 71.7, 71.4, 70.4, 70.0, 66.8, 66.5, 66.0, 65.8, 65.2, 62.8, 43.1, 41.4, 41.1, 38.6, 37.9, 37.6, 30.8, 29.8, 29.6, 29.1, 26.7; MS (LSIMS, glycerol/thioglycerol) 3369 (M + Na), 3152 (M – head).

(G8TrgP)$_4$mTet. From **(8TrgP)$_4$mTet** (40.0 mg, 15.7 μmol), as a clear oil (10.3 mg, 3.0 μmol, 19%): ^{13}C NMR, 90.57 MHz (CD_3OD) 173.5, 173.4, 172.1, 172.2, 170.6, 86.5, 85.8, 81.9, 79.6, 74.3, 71.6, 71.3, 70.0, 64.7, 66.4, 66.0, 65.2, 62.8, 43.1, 41.3, 41.1, 38.6, 37.8, 37.6, 29.9, 29.6, 29.1, 26.7; MS (LSIMS, glycerol) 3347 (M + H).

(G8TrgP)$_6$Hex. From **(8TrgP)$_6$Hex** (50.3 mg, 13.7 μmol), as a clear oil (32.0 mg, 6.5 μmol, 47%): ^{13}C NMR, 90.57MHz (CD_3OD) 173.5, 173.4, 172.9, 172.8, 172.2, 172.1, 172.0, 171.9, 170.8, 86.5, 85.8, 81.9, 81.8, 80.5, 79.6, 79.5, 74.3, 71.6, 71.3, 71.2, 70.0, 66.6, 66.5, 65.9, 65.8, 65.2, 62.9, 42.8, 42.7, 41.2, 38.5, 37.5, 37.4, 29.9, 29.6, 29.1, 26.7; MS (LSIMS, glycerol/thioglycerol) 4187 (M – wall), 3483 (M – 2wall), 2776 (M – 3wall).

(GTrg$_2$P)$_2$Di. From **(Trg$_2$P)$_2$Di** (71.0 mg, 50.0 μmol), as a clear oil (21.7 mg, 12.0 μmol, 24%): ^{13}C NMR, 90.57 MHz (CD_3OD) 173.4, 173.3, 173.1, 172.2, 171.9, 172.0, 171.7, 86.4, 85.6, 82.0, 79.9, 79.6, 79.5, 74.3, 71.6, 71.3, 71.2, 70.9, 70.4, 69.9, 66.1, 65.8, 65.3, 62.9, 42.9, 42.5, 41.1, 39.5, 38.6, 37.7, 37.5, 29.4, 28.9; MS (LSIMS, glycerol) 1108 (M – wall).

(GTrg$_2$P)$_4$Tet. From **(Trg$_2$P)$_4$Tet** (56.1 mg, 21.9 μmol), as a clear oil (19.5 mg, 5.8 μmol, 26%): ^{13}C NMR, 90.57 MHz (CD_3OD) 173.4, 173.2, 173.1, 173.0, 172.2, 172.1, 172.0, 171.9, 171.1, 86.4, 85.6, 82.0, 81.9, 79.9, 79.6, 79.5, 74.3, 71.3, 71.2, 70.5, 70.3, 71.6, 70.0, 66.0, 65.8, 65.3, 62.8, 42.9, 42.6, 41.1, 39.5, 38.6, 37.7, 37.5, 29.5, 29.4, 29.0; MS (LSIMS, glycerol) 1953 (M – 2wall).

(GTrg$_2$P)$_6$Hex. From **(Trg$_2$P)$_6$Hex** (17.0 mg, 4.5 μmol), as a clear oil (4.5 mg, 915 nmol, 20%): ^{13}C NMR, 90.57 MHz (CD_3OD) 173.4, 173.2, 172.2, 172.1, 172.0, 170.9, 86.4, 85.6, 82.0, 81.9, 80.5, 79.6, 79.5, 74.3, 71.3, 71.2, 71.6, 70.0, 66.1, 66.0, 65.8, 62.8, 42.9, 42.6, 41.1, 38.6, 37.7, 37.6, 29.8, 29.1.

(G5$_2$P)$_2$Di. From **(5$_2$P)$_2$Di** (26.7 mg, 21.5 μmol), as a clear oil (5.6 mg, 3.4 μmol, 16%): ^{13}C NMR, 90.57 MHz (CD_3OD) 173.0, 172.0, 171.1, 86.4, 85.8, 82.1, 82.0, 80.7, 79.6, 79.5, 74.3, 71.8, 71.7, 71.6, 66.5, 66.0, 65.0, 62.9, 43.0, 42.9, 41.1, 38.7, 37.7, 37.5, 29.5, 29.2, 27.7, 23.2; MS (LSIMS, thioglycerol) 1629 (M + H), 1318, 1016 (M – wall).

(G5$_2$P)$_4$Tet. From **(5$_2$P)$_4$Tet** (73.9 mg, 33.4 μmol), as a clear oil (4.0 mg, 1.3 μmol, 4%): ^{13}C NMR, 90.57 MHz (CD_3OD) 173.5, 173.4, 172.2, 172.1, 172.0, 171.2, 86.5, 85.7, 82.1, 82.0, 80.1, 79.8, 79.7, 74.5, 71.4, 71.3, 70.8, 70.4, 66.3, 66.2, 65.8, 65.4, 62.9, 43.0, 42.8, 41.2, 38.8, 38.0, 37.8, 30.4, 29.8, 29.0, 27.0; MS (LSIMS, thioglycerol) 2995 (M + H), 2684, 2382 (M – wall).

(G12$_2$P)$_2$Di. From **(12$_2$P)$_2$Di** (27.0 mg, 16.6 μmol), as a clear oil (6.7 mg, 3.3 μmol, 20%): ^{13}C NMR, 90.57 MHz (CD_3OD) 173.4, 173.3, 172.9, 172.2, 172.0, 171.9, 171.3, 86.4, 85.8, 82.0, 81.9, 80.3, 79.6, 79.5, 74.3, 71.4, 71.3, 71.2, 70.9, 66.8, 66.6, 66.5, 66.1, 65.2, 62.9, 43.0, 42.8, 41.2, 38.7, 37.9, 37.6, 30.8, 30.4, 29.8, 28.9, 27.1; MS (LSIMS, thioglycerol) 2022 (M + H), 2044 (M + Na), 1711, 1213 (M – wall).

(G12$_2$P)$_4$Tet. From **(12$_2$P)$_4$Tet** (55.0 mg, 18.3 μmol), as a colorless solid (10.4 mg, 2.8 μmol, 15%): ^{13}C NMR, 90.57 MHz (CD_3OD) 173.4, 172.9, 172.1, 171.9, 171.0, 86.5, 85.8, 82.1, 79.8, 79.7, 74.3, 71.4, 70.6, 66.6, 66.1, 65.6, 62.9, 43.0, 42.8, 41.3, 38.8, 37.7, 30.8, 30.5, 29.8, 29.0, 27.1; MS (LSIMS, glycerol) 3468, 2970 (M – wall).

General Procedure for the Addition of (Hydroxypropyl)-thio Head Groups (P). The appropriate **(YZP)$_n$Core** (30 μmol) and 3-mercapto-1-propanol (3 equiv per alkene) as a 2-propanol solution were added to 2-propanol (20 mL), piperidine (0.25 mL) was added, and the mixture was stirred at reflux for 1 h. The solvent was removed and the product dissolved in 4:3 chloroform/methanol (2 mL) and chromatographed by gel filtration (Sephadex LH 20, 4 × 20 cm). The product was collected in 1-mL fractions near the void volume. Product containing fractions were identified by TLC (silanized silica, Merck RP-2, 5% CH_3OH in $CHCl_3$ eluent, I_2 stain) and combined, and the solvent was removed to give **(PYZP)$_n$Core**. The ^{1}H NMR spectra of the products were recorded, but due to the large number of exchangeable protons were relatively uninformative. All spectra were consistent with complete Michael addition as evidenced by the lack of olefinic resonances. General features (δ, $CDCl_3$): 4.4–4.0, 3.7–3.5, 3.0–2.5, 2.0–1.8, 1.7–1.1.

(P8$_2$P)$_4$Tet. From **(8$_2$P)$_4$Tet** (70.0 mg, 27.5 μmol), as a pale yellow oil (36.6 mg, 12.6 μmol, 46%): ^{13}C NMR, 62.89 MHz (δ, $CDCl_3$) 171.5, 171.2, 170.3, 169.2, 80.0, 71.5, 70.3, 65.5, 65.0, 63.5, 61.2, 41.9, 41.7, 31.9, 29.1, 28.5, 27.9, 25.8; MS (LSIMS, glycerol) 2915 (M + H), 2824.

(P8TrgP)$_4$Tet. From **(8TrgP)$_4$Tet** (71.1 mg, 27.8 μmol), as a pale yellow oil (34.8 mg, 11.8 μmol, 42%): ^{13}C NMR, 90.57 MHz (δ, $CDCl_3$) 171.5, 171.4, 171.3, 171.2, 170.3, 170.2, 169.1, 79.9, 71.3, 70.2, 70.5, 68.9, 65.3, 64.9, 64.3, 63.9, 63.5, 60.9, 41.7, 41.6, 41.4, 36.5, 36.4, 36.3, 31.8, 31.7, 28.7, 28.6, 28.3, 28.0, 27.9, 27.7, 25.4, 25.3; MS (LSIMS, glycerol) 2831 (M + H), 2842.

(P8TrgP)$_6$Hex. From **(8TegP)$_6$Hex** (90.0 mg, 24.3 μmol), as a yellow oil (33.8 mg, 7.9 μmol, 33%): ^{13}C NMR, 90.57 MHz (δ, $CDCl_3$) 171.6, 171.5, 171.3, 171.2, 170.4, 170.3, 169.1, 80.0, 70.5, 68.9, 65.4, 64.9, 64.4, 63.9, 63.6, 61.0, 41.8, 41.7, 36.6, 36.5, 36.4, 31.9, 31.8, 28.8, 28.4, 28.1, 28.0, 27.8, 25.5, 25.4, 25.3; MS (LSIMS, glycerol) 4264 (M + H), 4173.

General Procedure for Addition of Thioacetate Head Groups (A). The appropriate **(YZP)$_n$Core** (30 μmol) and mercaptoacetic acid (3 equiv per alkene) as a 2-propanol solution were added to tetrahydrofuran (20 mL) at 50 °C, 2,2,6,6-tetramethylpiperidine (0.25 mL, pH 8) was added, and the mixture was stirred a further 3 h. The solvent was removed and the product dissolved in 4:3 chloroform/methanol (2 mL) and added to a Dowex 50 × 8–100 ion-exchange resin (1 × 5 cm) column, which had been activated with 2 M sulfuric acid and washed to neutral with water, methanol (50 mL), and 4:3 chloroform/methanol (50 mL). The acidic fractions were combined and concentrated to about 1 mL and chromatographed by gel filtration (Sephadex LH 20, 4 × 20 cm). The product was collected in 1-mL fractions near the void volume. Product-containing fractions were identified by TLC (silanized silica, Merck RP-2, 5% CH_3OH in $CHCl_3$ eluent, I_2 stain) and combined, and the solvent was removed to give **(AYZP)$_n$Core**. The ^{1}H NMR spectra of the products were recorded, but due to the large number of exchangeable protons were relatively uninformative. All spectra were consistent with complete Michael addition as evidenced by the lack of olefinic resonances. General features (δ, $CDCl_3$): 4.4–4.0, 3.7–3.5, 3.0–2.5, 2.0–1.8, 1.7–1.1.

(A8$_2$P)$_4$Tet. From **(8$_2$P)$_4$Tet** (68.0 mg, 26.7 μmol), as a yellow oil (32.0 mg, 10.9 μmol, 41%): ^{13}C NMR, 90.57 MHz (δ, $CDCl_3$) 173.3, 171.2, 170.8, 170.4, 170.3, 170.0, 169.2, 79.9, 71.3, 70.2, 65.6, 65.5, 65.0, 63.5, 41.8, 41.6, 36.5, 36.2, 33.0, 29.0, 28.4, 28.1, 27.9,

25.7, 25.6; MS (LSIMS, thioglycerol) 2915 (M + H), 2937, 2959, 2981 (M + *n*Na), 2824 (M − head), 2846, 2868, 2890 (M + *n*Na − head).

(A8TrgP)$_4$Tet. From **(8TrgP)$_4$Tet** (80.9 mg, 31.6 μmol), as a yellow oil (19.2 mg, 6.5 μmol, 21%): ^{13}C NMR, 90.57 MHz (δ, $CDCl_3$) 173.3, 171.0, 170.5, 169.2, 79.0, 71.3, 70.2, 70.5, 68.8, 65.5, 65.4, 64.9, 64.6, 64.0, 63.7, 42.2, 41.6, 41.5, 36.3, 35.9, 33.7, 33.0, 28.6, 28.5, 28.3, 28.0, 27.9, 25.4, 25.3; MS (LSIMS, thioglycerol) 2953, 2997, 3015 (M + *n*Na), 2840 (M − head), 2862, 2884, 2906 (M + *n*Na − head).

(A8TrgP)$_6$Hex. From **(8TrgP)$_6$Hex** (48.0 mg, 12.9 μmol), as a yellow oil (12.1 mg, 2.8 μmol, 22%): ^{13}C NMR, 90.57 MHz (δ, $CDCl_3$) 171.9, 171.4, 171.2, 170.4, 169.0, 169.0, 79.9, 70.4, 70.3, 69.3, 68.9, 65.6, 65.4, 64.9, 64.7, 64.4, 64.0, 63.6, 42.3, 41.7, 36.3, 35.9, 33.6, 28.3, 28.1, 27.9, 25.6, 25.3; MS (LSIMS, thioglycerol) 4173 (M − head), 4145 (M + Na − head).

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Appendix. List of Compound Name Abbreviations

	Acyclic Compounds
8MA$_2$	5,14-dioxa-4,15-dioxooctadeca-2,16-diene-1,18-dicarboxylic acid
5MA$_2$	5,11-dioxa-4,12-dioxopentadeca-2,13-diene-1,15-dicarboxylic acid
Ur(OH)$_2$	*N,N'*-bis(3-hydroxypropyl)urea
PhgCl$_2$	1,3-bis(chloroacetamido)benzene
	Macrocyclic Dienes
8$_2$	1,6,15,20-tetraoxa-2,5,16,19-tetraoxocyclooctacosa-3,17-diene
8Trg	1,6,9,12,15,20-hexaoxa-2,5,16,19-tetraoxocyclooctacosa-3,17-diene
Trg$_2$	1,6,9,12,15,20,23,24-octaoxa-2,5,16,19-tetraoxocyclooctacosa-3,17-diene (Trg$_2$)
5$_2$	1,6,12,17-tetraoxa-2,5,13,16-tetraoxocyclodicosa-3,14-diene
12$_2$	1,6,19,24-tetraoxa-2,5,20,23-tetraoxocyclohexatriconta-3,21-diene (12$_2$)
Ur$_2$	10,12,25,27-tetraaza-1,6,16,21-tetraoxa-2,5,11,17,20,26-hexaoxocyclotricosa-3,18-diene
8Ur	10,12-diaza-1,6,16,21-tetraoxa-2,5,11,17,20-pentaoxocyclononacosa-3,18-diene
8Phg	2,27-diaza-5,10,19,24-tetraoxa-6,9,20,23-tetraoxobicyclo[26.3.1]dotriaconta-1,7,21,28,30-pentaene
	Wall Units
8$_2$POH	3-(4-hydroxy-1-thiabutyl)-1,6,15,20-tetraoxa-2,5,16,19-tetraoxocyclooctacos-17-ene
8$_2$POMs	3-[4-(methylsulfonyl)-1-thiabutyl]-1,6,15,20-tetraoxa-2,5,16,19-tetraoxocyclooctacos-17-ene
8$_2$PI	3-(4-iodo-1-thiabutyl)-1,6,15,20-tetraoxa-2,5,16,19-tetraoxocyclooctacos-17-ene
8TrgPOH	3- and 4-(4-hydroxy-1-thiabutyl)-1,6,9,12,15,20-hexaoxa-2,5,16,19-tetraoxocyclooctacos-17-ene
8TrgPOMs	3- and 4-(4-methylsulfonyl-1-thiabutyl)-1,6,9,12,15,20-hexaoxa-2,5,16,19-tetraoxocyclooctacos-17-ene
8TrgPI	3- and 4-(4-iodo-1-thiabutyl)-1,6,9,12,15,20-hexaoxa-2,5,16,19-tetraoxocyclooctacos-17-ene
TrgPOH	3-(4-hydroxy-1-thiabutyl)-1,6,9,12,15,20,23,24-octaoxa-2,5,16,19-tetraoxocyclooctacos-3,17-ene
Trg$_2$POMs	3-(4-methylsulfonyl-1-thiabutyl)-1,6,9,12,15,20,23,24-octaoxa-2,5,16,19-tetraoxocyclooctacos-17-ene
Trg$_2$PI	3-(4-iodo-1-thiabutyl)-1,6,9,12,15,20,23,24-octaoxa-2,5,16,19-tetraoxocyclooctacos-17-ene
5$_2$POH	3-(4-hydroxy-1-thiabutyl)-1,6,12,17-tetraoxa-2,5,13,16-tetraoxocyclodicos-14-ene
5$_2$POMs	3-(4-methylsulfonyl-1-thiabutyl)-1,6,12,17-tetraoxa-2,5,13,16-tetraoxocyclodicos-14-ene
5$_2$PI	3-(4-iodo-1-thiabutyl)-1,6,12,17-tetraoxa-2,5,13,16-tetraoxocyclodicos-14-ene
12$_2$POH	3-(4-hydroxy-1-thiabutyl)-1,6,19,24-tetraoxa-2,5,20,23-tetraoxocyclohexatricont-21-ene
12$_2$POMs	3-(4-methylsulfonyl-1-thiabutyl)-1,6,19,24-tetraoxa-2,5,20,23-tetraoxocyclohexatricont-21-ene
12$_2$PI	3-(4-iodo-1-thiabutyl)-1,6,19,24-tetraoxa-2,5,20,23-tetraoxocyclohexatricont-21-ene
	Wall Plus Core (Crown Ether Ester Polyenes)
(8$_2$P)$_2$Di	bis[[3-(1,6,15,20-tetraoxa-2,5,16,19-tetraoxocyclooctacos-17-enyl)]-4-thiabutyl] (2*R*,3*R*)-1,4,7,10,13,16-hexaoxacyclooctadecane-2,3-dicarboxylate
(8$_2$P)$_4$Tet	tetrakis[[3-(1,6,15,20-tetraoxa-2,5,16,19-tetraoxocyclooctacos-17-enyl)]-4-thiabutyl] (2*R*,3*R*,11*R*,12*R*)-1,4,7,10,13,16-hexaoxacyclooctadecane-2,3,11,12-tetracarboxylate
(8$_2$P)$_6$Hex	hexakis[[3-(1,6,15,20-tetraoxa-2,5,16,19-tetraoxocyclooctacos-17-enyl)]-4-thiabutyl] (2*R*,3*R*,8*R*,9*R*,14*R*,15*R*)-1,4,7,10,13,16-hexaoxacyclooctadecane-2,3,8,9,14,15-hexacarboxylate
(8TrgP)$_2$Di	bis[[3- and 4-(1,6,9,12,15,20-hexaoxa-2,5,16,19-tetraoxocyclooctacos-17-enyl)]-4-thiabutyl] (2*R*,3*R*)-1,4,7,10,13,16-hexaoxacyclooctadecane-2,3-dicarboxylate
(8TrgP)$_2$mDi	bis[[3- and 4-(1,6,9,12,20-hexaoxa-2,5,16,19-tetraoxocyclooctacos-17-enyl)]-4-thiabutyl] (2*R*,3*S*)-1,4,7,10,13,16-hexaoxacyclooctadecane-2,3-dicarboxylate
(8TrgP)$_4$Tet	tetrakis[[3- and 4-(1,6,9,12,15,20-hexaoxa-2,5,16,19-tetraoxocyclooctacos-17-enyl)]-4-thiabutyl] (2*R*,3*R*,11*R*,12*R*)-1,4,7,10,13,16-hexaoxacyclooctadecane-2,3,11,12-tetracarboxylate
(8TrgP)$_4$mTet	tetrakis[[3- and 4-(1,6,9,12,15,20-hexaoxa-2,5,16,19-tetraoxocyclooctacos-17-enyl)]-4-thiabutyl] (2*R*,3*S*,11*R*,12*S*)-1,4,7,10,13,16-hexaoxacyclooctadecane-2,3,11,12-tetracarboxylate
(8TrgP)$_6$Hex	hexakis[[3- and 4-(1,6,9,12,15,20-hexaoxa-2,5,16,19-tetraoxocyclooctacos-17-enyl)]-4-thiabutyl] (2*R*,3*R*,8*R*,9*R*,14*R*,15*R*)-1,4,7,10,13,16-hexaoxacyclooctadecane-2,3,8,9,14,15-hexacarboxylate
(Trg$_2$P)$_2$Di	bis[[3-(1,6,9,12,15,20,23,24-octaoxa-2,5,16,19-tetraoxocyclooctacos-17-enyl)]-4-thiabutyl] (2*R*,3*R*)-1,4,7,10,13,16-hexaoxacyclooctadecane-2,3-dicarboxylate
(Trg$_2$P)$_4$Tet	tetrakis[[3-(1,6,9,12,15,20,23,24-octaoxa-2,5,16,19-tetraoxocyclooctacos-17-enyl)]-4-thiabutyl] (2*R*,3*R*,11*R*,12*R*)-1,4,7,10,13,16-hexaoxacyclooctadecane-2,3,11,12-tetracarboxylate
(Trg$_2$P)$_6$Hex	hexakis[[3-(1,6,9,12,15,20,23,24-octaoxa-2,5,16,19-tetraoxocyclooctacos-17-enyl)]-4-thiabutyl] (2*R*,3*R*,8*R*,9*R*,14*R*,15*R*)-1,4,7,10,13,16-hexaoxacyclooctadecane-2,3,8,9,14,15-hexacarboxylate
(5$_2$P)$_2$Di	bis[[3-(1,6,12,17-tetraoxa-2,5,13,16-tetraoxocyclodicos-14-enyl)-4-thiabutyl) (2*R*,3*R*)-1,4,7,10,13,16-hexaoxacyclooctadecane-2,3-dicarboxylate
(5$_2$P)$_2$Di	tetrakis[[3-(1,6,12,17-tetraoxa-2,5,13,16-tetraoxocyclodicos-14-enyl)]-4-thiabutyl] (2*R*,3*R*,11*R*,12*R*)-1,4,7,10,13,16-hexaoxacycloctadecane-2,3,11,12-tetracarboxylate
(12$_2$P)$_2$Di	bis[[3-(1,6,19,24-tetraoxa-2,5,20,23-tetraoxocyclohexatricont-21-enyl)]-4-thiabutyl] (2*R*,3*R*)-1,4,7,10,13,16-hexaoxacyclooctadecane-2,3-dicarboxylate
(12$_2$P)$_4$Tet	tetrakis[[3-(1,6,19,24-tetraoxa-2,5,20,23-tetraoxocyclohexatricont-21-enyl)]-4-thiabutyl] (2*R*,3*R*,11*R*,12*R*)-1,4,7,10,13,16-hexaoxacyclooctadecane-2,3,11,12-tetracarboxylate

Complete Ion Channel Mimics

(G8$_2$P)$_2$Di	bis[[3-[17- and/or 18-(β-D-glucopyranosylthio)-1,6,15,20-tetraoxa-2,5,16,19-tetraoxocyclooctacosyl]]-4-thiabutyl] (2*R*,3*R*)-1,4,7,10,13,16-hexaoxacyclooctadecane-2,3-dicarboxylate
(G8$_2$P)$_4$Tet	tetrakis[[3-[17- and/or 18-(β-D-glucopyranosylthio)-1,6,15,20-tetraoxa-2,5,16,19-tetraoxocyclooctacosyl]]-4-thiabutyl] (2*R*,3*R*,11*R*,12*R*)-1,4,7,10,13,16-hexaoxacyclooctadecane-2,3,11,12-tetracarboxylate
(G8$_2$P)$_6$Hex	hexakis[[3-[17- and/or 18-(β-D-glucopyranosylthio)-1,6,15,20-tetraoxa-2,5,16,19-tetraoxocyclooctacosyl]]-4-thiabutyl] (2*R*,3*R*,8*R*,9*R*,14*R*,15*R*)-1,4,7,10,13,16-hexaoxacyclooctadecane-2,3,8,9,14,15-hexacarboxylate
(G8TrgP)$_2$Di	bis[[3- and/or 4-(17- and/or 18-(β-D-glucopyranosylthio)-1,6,9,12,20-hexaoxa-2,5,16,19-tetraoxocyclooctacosyl]]-4-thiabutyl] (2*R*,3*R*)-1,4,7,10,13,16-hexaoxacyclooctadecane-2,3-dicarboxylate
(G8TrgP)$_2$mDi	bis[[3- and/or 4-[17- and/or 18-(β-D-glucopyranosylthio)-1,6,9,12,15,20-hexaoxa-2,5,16,19-tetraoxocyclooctacosyl]]-4-thiabutyl] (2*R*,3*S*)-1,4,7,10,13,16-hexaoxacyclooctadecane-2,3-dicarboxylate
(G8TrgP)$_4$Tet	tetrakis[[3- and/or 4-[17- and/or 18-(β-D-glucopyranosylthio)-1,6,9,12,15,20-hexaoxa-2,5,16,19-tetraoxocyclooctacosyl]]-4-thiabutyl] (2*R*,3*R*,11*R*,12*R*)-1,4,7,10,13,16-hexaoxacyclooctadecane-2,3,11,12-tetracarboxylate
(G8TrgP)$_4$mTet	tetrakis[[3- and/or 4-[17- and/or 18-(β-D-glucopyranosylthio)-1,6,9,12,15,20-hexaoxa-2,5,16,19-tetraoxocyclooctacosyl]]-4-thiabutyl] (2*R*,*SR*,11*R*,12*S*)-1,4,7,10,13,16-hexaoxacyclooctadecane-2,3,11,12-tetracarboxylate
(G8TrgP)$_6$Hex	hexakis[[3- and/or 4-[17- and/or 18-(β-D-glucopyranosylthio)-1,6,9,12,15,20-hexaoxa-2,5,16,19-tetraoxocyclooctacosyl]]-4-thiabutyl] (2*R*,3*R*,8*R*,9*R*,14*R*,15*R*)-1,4,7,10,13,16-hexaoxacyclooctadecane-2,3,8,9,14,15-hexacarboxylate
(GTrg$_2$P)$_2$Di	bis[[3-[17- and/or 18-(β-D-glucopyranosylthio)-1,6,9,12,15,20,23,24-octaoxa-2,5,16,19-tetraoxocyclooctacosyl]]-4-thiabutyl] (2*R*,3*R*)-1,4,7,10,13,16-hexaoxacyclooctadecane-2,3-dicarboxylate
(GTrg$_2$P)$_6$Hex	hexakis[[3-[17- and/or 18-(β-D-glucopyranosylthio)-1,6,9,12,15,20,23,24-octaoxa-2,5,16,19-tetraoxocyclooctacosyl]]-4-thiabutyl] (2*R*,3*R*,8*R*,9*R*,14*R*,15*R*)-1,4,7,10,13,16-hexaoxacyclooctadecane-2,3,8,9,14,15-hexacarboxylate
(G5$_2$P)$_2$Di	bis[[3-[14- and/or 15-(β-D-glucopyranosylthio)-1,6,12,17-tetraoxa-2,5,13,16-tetraoxocyclodicosyl]]-4-thiabutyl] (2*R*,3*R*)-1,4,7,10,13,16-hexaoxacyclooctadecane-2,3-dicarboxylate
(G5$_2$P)$_4$Tet	tetrakis[[3-[14- and/or 15-(β-D-glucopyranosylthio)-1,6,12,17-tetraoxa-2,5,13,16-tetraoxocyclodicosyl]]-4-thiabutyl] (2*R*,3*R*,11*R*,12*R*)-1,4,7,10,13,16-hexaoxacyclooctadecane-2,3,11,12-tetracarboxylate
(G12$_2$P)$_2$Di	bis[[3-[21- and/or 22-(β-D-glucopyranosylthio)-1,6,19,24-tetraoxa-2,5,20,23-tetraoxocyclohexatricontyl]]-4-thiabutyl] (2*R*,3*R*)-1,4,7,10,13,16-hexaoxacyclooctadecane-2,3-dicarboxylate
(G12$_2$P)$_4$Tet	tetrakis[[3-[21- and/or 22-(β-D-glucopyranosylthio)-1,6,19,24-tetraoxa-2,5,20,23-tetraoxocyclohexatricontyl]]-4-thiabutyl] (2*R*,3*R*,11*R*,12*R*)-1,4,7,10,13,16-hexaoxacyclooctadecane-2,3,11,12-tetracarboxylate
(P8$_2$P)$_4$Tet	tetrakis[[3-[17- and/or 18-(4-hydroxy-1-thiabutyl)-1,6,15,20-tetraoxa-2,5,16,19-tetraoxocyclooctacosyl]]-4-thiabutyl] (2*R*,3*R*,11*R*,12*R*)-1,4,7,10,13,16-hexaoxacyclooctadecane-2,3,11,12-tetracarboxylate
(P8TrgP)$_4$Tet	tetrakis[[3- and/or 4-[17- and/or 18-(4-hydroxy-1-thiabutyl)-1,6,9,12,15,20-hexaoxa-2,5,16,19-tetraoxocyclooctacosyl]]-4-thiabutyl)] (2*R*,3*R*,11*R*,12*R*)-1,4,7,10,13,16-hexaoxacyclooctadecane-2,3,11,12-tetracarboxylate
(P8TrgP)$_6$Hex	hexakis[[3- and/or 4-[17- and/or 18-(4-hydroxy-1-thiabutyl)-1,6,9,12,15,20-hexaoxa-2,5,16,19-tetraoxocyclooctacosyl]]-4-thiabutyl] (2*R*,3*R*,8*R*,9*R*,14*R*,15*R*)-1,4,7,10,13,16-hexaoxacyclooctadecane-2,3,8,9,14,15-hexacarboxylate
(A8$_2$P)$_4$Tet	tetrakis[[3-[17- and/or 18-(1-thio-2-carboxyethyl)-1,6,15,20-tetraoxa-2,5,16,19-tetraoxocyclooctacosyl]]-4-thiabutyl] (2*R*,3*R*,11*R*,12*R*)-1,4,7,10,13,16-hexaoxacyclooctadecane-2,3,11,12-tetracarboxylate
(A8TrgP)$_4$Tet	tetrakis[[3- and/or 4-(17- and/or 18-(1-thio-2-carboxyethyl)-1,6,9,12,15,20-hexaoxa-2,5,16,19-tetraoxocyclooctacosyl]]-4-thiabutyl] (2*R*,3*R*,11*R*,12*R*)-1,4,7,10,13,16-hexaoxacyclooctadecane-2,3,11,12-tetracarboxylate
(A8TrgP)$_6$Hex	hexakis[[3- and/or 4-[17- and/or 18-(1-thia-2-carboxyethyl)-1,6,9,12,15,20-hexaoxa-2,5,16,19-tetraoxocyclooctacosyl]]-4-thiabutyl] (2*R*,3*R*,8*R*,9*R*,14*R*,15*R*)-1,4,7,10,13,16-hexaoxacyclooctadecane-2,3,8,9,14,15-hexacarboxylate