Synthesis of Amphiphilic Poly(*p*-phenylene)s with Pendant Dendrons and Linear Chains

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ABSTRACT: The Suzuki polycondensation of the amphiphilically equipped dibromobenzene derivatives **8** and **11** with benzene diboronic acid ester **12** to the new kind of polymeric amphiphiles **13** and **14** is described. They carry at each repeat unit either a hydrophobic alkyl chain and a hydrophilic dendron with oligoethyleneoxy chains (**13**) or a hydrophobic third generation Fréchet-type dendron and an oligoethyleneoxy chain (**14**). Some aspects of the behavior of these four compounds at the air/water interface and on mica are also reported.

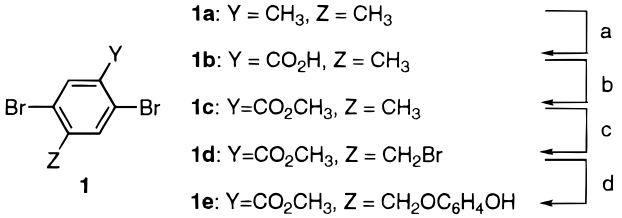
Introduction

The use of dendritic molecules as nanoscale building blocks for the construction of novel functional materials is a fascinating research topic in current chemistry.[1] Particular interest focuses on macromolecules that can be considered hybrids of dendritic and linear chain elements. Under structural aspects these macromolecules can be divided into two subclasses: those in which a linear backbone carries one or two dendrons at one or both termini[2] and others in which polymers are decorated with appendant dendrons at each repeat unit (r.u.).[3] The topology of some of the former is reminiscent of dumbbells and the latter of molecular cylinders. Amphiphilic representatives of both classes have been studied under colloid aspects as well as for their behavior at the air/water interface and on solid surfaces.[4] For a poly(*p*-phenylene) (PPP) derivative with both a hydrophobic and a hydrophilic dendron at each r.u. evidence for the dendrons' segregation into homophilic domains was obtained, which are oriented lengthwise along the backbone.[5] This kind of segregation differs from that of amphiphilic block copolymers where the homophilic domains are oriented perpendicular to the main chain. In this paper we report two novel amphiphilically equipped PPPs carrying both a pendant dendron and a flexible chain at each r.u. with either the dendron being hydrophobic and the chain hydrophilic or the other way around. Initial investigations into the behavior of these PPPs on the Langmuir trough are also reported. Some steps of the synthetic sequences have already been communicated;[5] a full account will be provided here.

Results and Discussion

The schemes are divided into (a) the synthesis of the unsymmetrically substituted dibromobenzenes **1d** and **1e** as core parts of the final monomers (Scheme 1), (b) the synthesis of the hydrophilic second generation (G2) dendron **5c** (Scheme 2), (c) the assembly of monomer **8** from **1d**, **5c**, and the hydrophobic chain **6** with attached hydroquinone linker (Scheme 3), (d) the assembly of monomer **11** from **1e** modified by an oligoethyleneoxy chain and Fréchet-type G3 dendron **9b** carrying a hydroquinone linker (Scheme 4), and the polymerizations of monomers **8** and **11** with benzene diboronic acid ester **12** to give the amphiphilically equipped poly(*p*-phenylene)s **13** and **14**, respectively. The general idea behind the chemistry used is that it should be simple and high yielding in order to provide facile access to the targeted polymers. The following comments are nevertheless appropriate.

Scheme 1[a]



[a] (a) 45% HNO_3, 100 °C, 7 days, 82%; (b) CH_3OH, H_2SO_4 (cat.), reflux for 8 h, 87%; (c) CH_2Cl_2, Br_2, UV light, 15 °C, 66%; (d) hydroquinone, K_2CO_3, acetone, reflux for 24 h, 77%.

The methyl group oxidation of **1a** is not fully selective (Scheme 1).[6] A few percent of dioxidation product (not shown) is formed which can be separated by column chromatography. It is more convenient however to carry the sequence through to **1e** (or **1d** on route to **8**) and do the purification then. Compound **1e** was obtained on the 20 g scale. Bromination of **1c** with NBS in tetrachloromethane was inferior to the usage of bromine at 20 °C under UV irradiation (30% versus 70% yield of **1d**). The hydrophilic G2 dendron **5c** was obtained on the 6 g scale (Scheme 2). Its purification required repeated column chromatography. Despite several attempts, correct data from microanalysis could not be obtained for it. Brominations of **4b** and **5b** turned out to be most convenient under Appel conditions. The reduction of **7a** to **7b** and **10a** to **10b** was done with borohydride instead of LAH because debromination would otherwise occurs (Scheme 3). Monomer **8** was obtained as analytically pure material on the 3−4 g scale. The lyophilization was done under ice cooling from benzene to prevent melting. The SEC trace shows a monomodal peak with narrow

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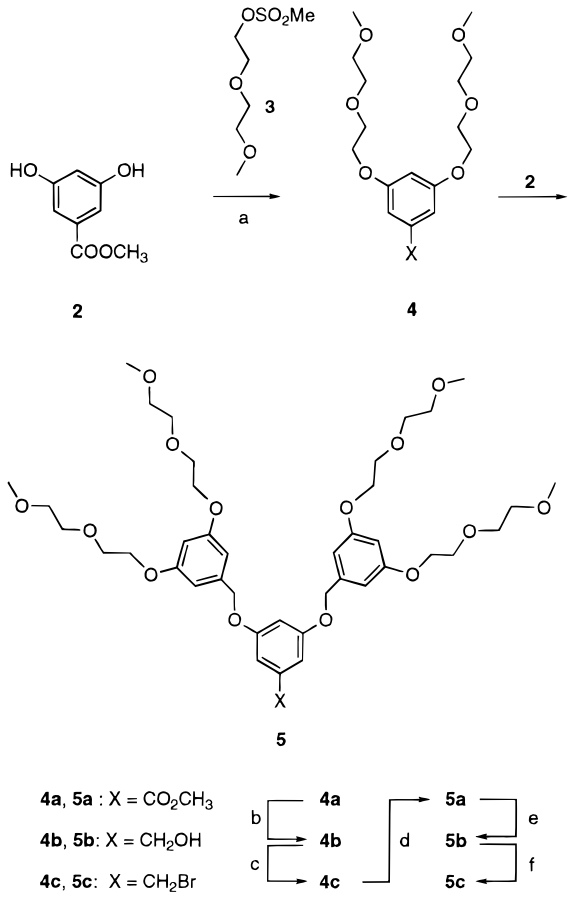
Scheme 2[a]



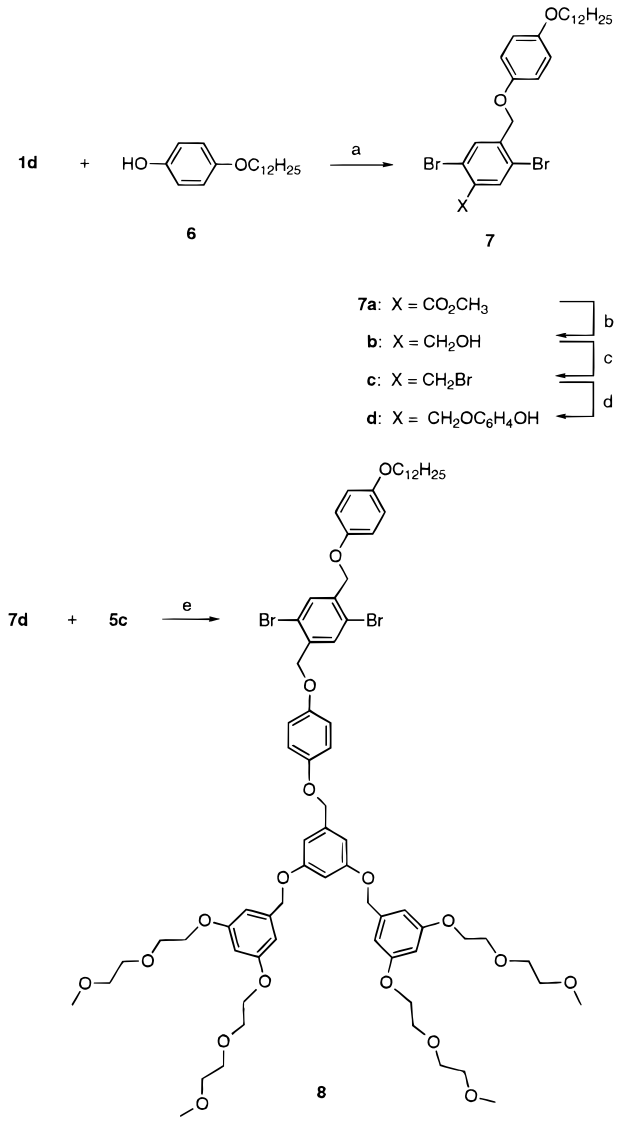
[a] (a) DMF, K_2CO_3, 90 °C, 48 h, 62%; (b) $LiAlH_4$, THF, r.t. for 24 h, 86%; (c) PPh_3, CBr_4, THF, r.t. for 1 h, 76%; (d) K_2CO_3, acetone, reflux for 24 h, 99%; (e) like (b), 88%; (f) like (c), 61%.

distribution ($M_w/M_n = 1.01$). After reacting dendron **9a** with hydroquinone, quinone impurities were removed by washing with aqueous borohydride solution (Scheme 4). Monomer **11** was obtained as analytically pure material on the 3−4 g scale. Its SEC trace is monomodal with narrow distribution ($M_w/M_n = 1.01$). Its purity was checked by 500 MHz NMR spectroscopy and found to be better than 98%.

Suzuki polycondensations (SPC)[7] were done with diboronic acid ester **12** using standard conditions in THF. Freshly prepared $Pd(PPh_3)_4$ and $Pd[P(p\text{-tolyl})_3]_3$ were used as catalyst precursors. The results are summarized in Table 1. The molecular weights were determined by SEC referenced to polystyrene standard, a method which is known to underestimate the molecular weights of polymers with pendent dendrons of up to at least generation G3 considerably.[8]

Monomers **8** and **11** and polymers **13** (GPC: Pn = 20) and **14** were investigated at the air/water interface using a Langmuir trough.[9] For the monomeric compounds **8** and **11**, surface pressure−area isotherms at room temperature reveal stable monolayers up to 15 mN/m or more with an area change of less than 1% during 20 min (Figure 1). The area per molecule of **8** at 20 mN/m is about 0.70 nm^2/molecule, very similar to a related molecule with the same hydrophilic headgroup but a different hydrophobic tail.[5] The isotherm of **11** is considerably steeper with a larger area in the condensed state of 1.0 nm^2/molecule at 15 mN/m. Polymer **13** forms monolayers that are less stable (area change of more

Scheme 3[a]

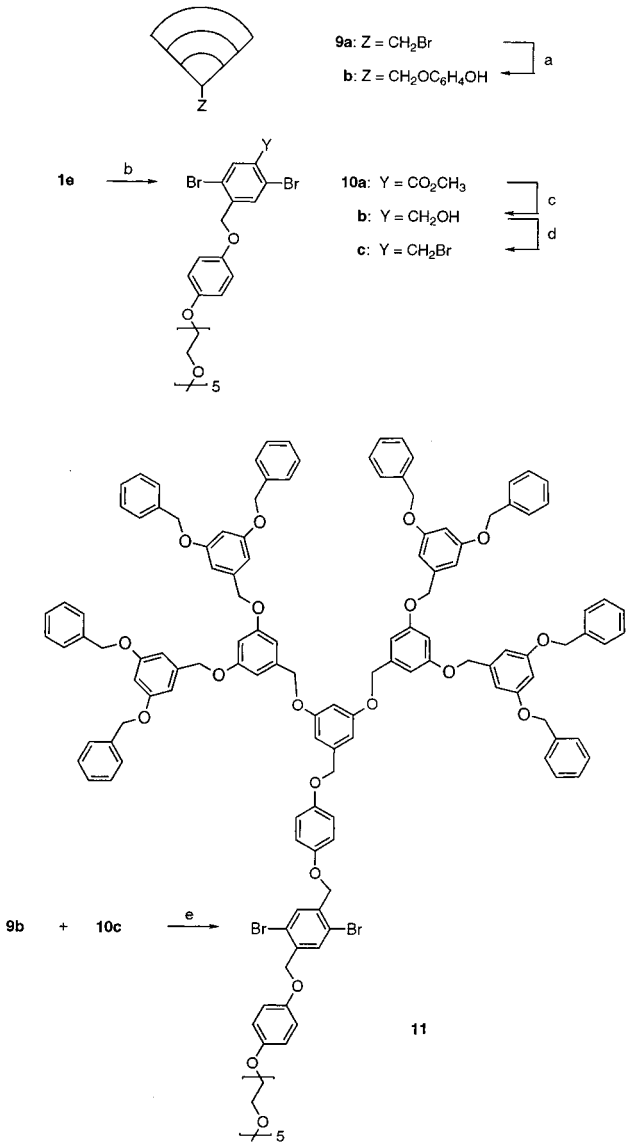


[a] (a) K_2CO_3, acetone, reflux for 24 h, 85%; (b) $LiBH_4$, THF, reflux for 8 h, 86%; (c) PPh_3, CBr_4, THF, r.t. for 1 h, 74%; (d) like (a), 62%; (e) like (a), 79%.

than 5% during 20 min). The surface area isotherm reveals a small hysteresis and an area per molecule slightly larger than the corresponding monomeric compound **8** (Figure 1). Since polymer **14** does not form a reproducible isotherm, only compounds **8**, **11**, and **13** were transferred to mica by the Langmuir−Blodgett technique with a transfer efficiency >95%.

The freshly transferred monolayers of **11** are homogeneous with a few holes with a diameter of approximately 50 nm at a separation of approximately 1 μm. On the time scale of days at 20 °C the holes expand, and aggregates form on top (Figure 2, top to bottom). The film of monomer **8** transferred at lower pressure is stable but heterogeneous with a considerable fraction of the surface uncovered. At 20 mN/m the film is initially homogeneous. Upon annealing at 20 °C at a time scale of days, holes are formed, and the film thickness increases gradually from 1.8 to 2.8 nm after 2 days. There is no aggregate formation on top of the film. The transferred films of **13** exhibit stable, rather smooth monolayers, whose morphology remains unchanged for at least a week. Only in the case of **13** some

Scheme 4[a]



[a] (a) Hydroquinone, K_2CO_3, acetone, reflux for 24 h, 71%; (b) DMF, K_2CO_3, 18-crown-6, KI, 90 °C, 24 h; (c) $LiBH_4$, THF, reflux for 8 h, 94%; (d) PPh_3, CBr_4, THF, r.t. for 1 h, 84%; (e) K_2CO_3, acetone, reflux for 24 h, 71%.

molecular scale resolution of the transferred films could be observed by scanning force microscopy. Linear features of 3.7 nm can be attributed to the molecular cross section. This matter is presently under investigation.

Both monomers are stable on water but not on mica which may reflect the discrepancy of the space demand of the hydrophilic and hydrophobic parts. Polymer **13**, however, is stable on mica which shows that the covalent attachment of amphiphilic repeat units can stabilize a LB monolayer. The fact that polymer **14** does not form a stable monolayer, not even on water, indicates that this polymer with its amphiphilic misbalance does not behave like an amphiphile under these conditions. Polymer **13** closely resembles a recently prepared amphiphilic PPP derivative[5] with the same hydrophilic unit in regard to not only its surface behavior but also its space demand per repeat unit which is approximately 0.75 nm^2/r.u.

The differential scanning calorimetry curve of the second and third heating/cooling cycle (10 K/min) for polymer **13** showed a second-order transition at 130 °C

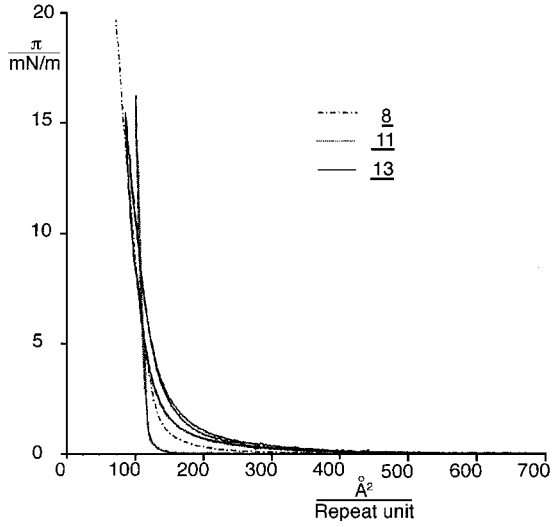


Figure 1. Surface pressure−area isotherms at the air/water interface of monomers **8** and **11** and polymer **13**.

Scheme 5. $NaHCO_3$, THF, H_2O, 1−1.5 mol % $Pd[P(p\text{-tolyl})_3]_3$, Reflux for 3 days

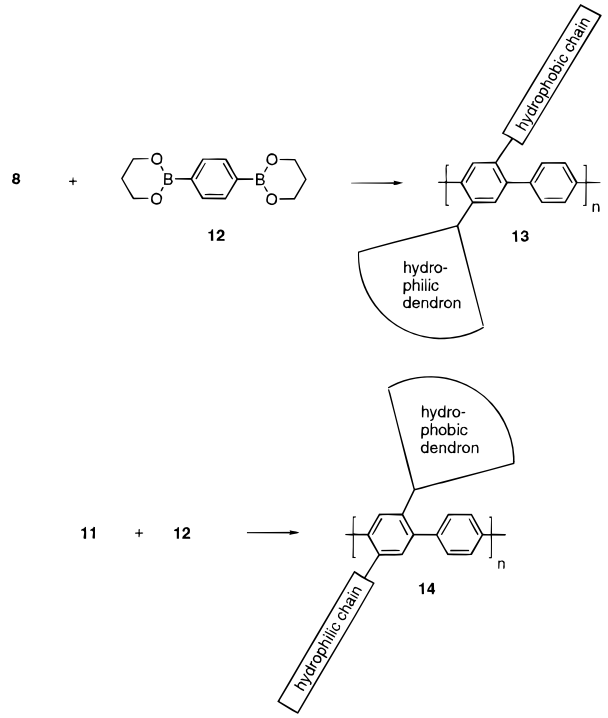


Table 1. Yields and Molecular Weights (GPC versus PS) of Polymers 13 and 14 Prepared

entry	monomer	amt prepared (mg)	yield [%]	M_n [kDa]	Pn	M_w [kDa]	Pw	PD
1	**8**	**13** (730)	95	56	42	130	97	2.3
2	**8**	**13** (300)	97	28	20	57	40	2.0
3	**11**	**14** (620)	94	21	10	39	18	1.9
4	**11**	**14** (706)	91	25	11	48	22	1.9

which may be attributed to a side chain or backbone glass transition. For polymer **14** a related transition could not be identified with certainty.

Conclusion and Outlook

The amphiphilic Suzuki-type monomers **8** and **11** undergo SPC to PPP derivatives **13** and **14** whose structure can be described as a string of covalently

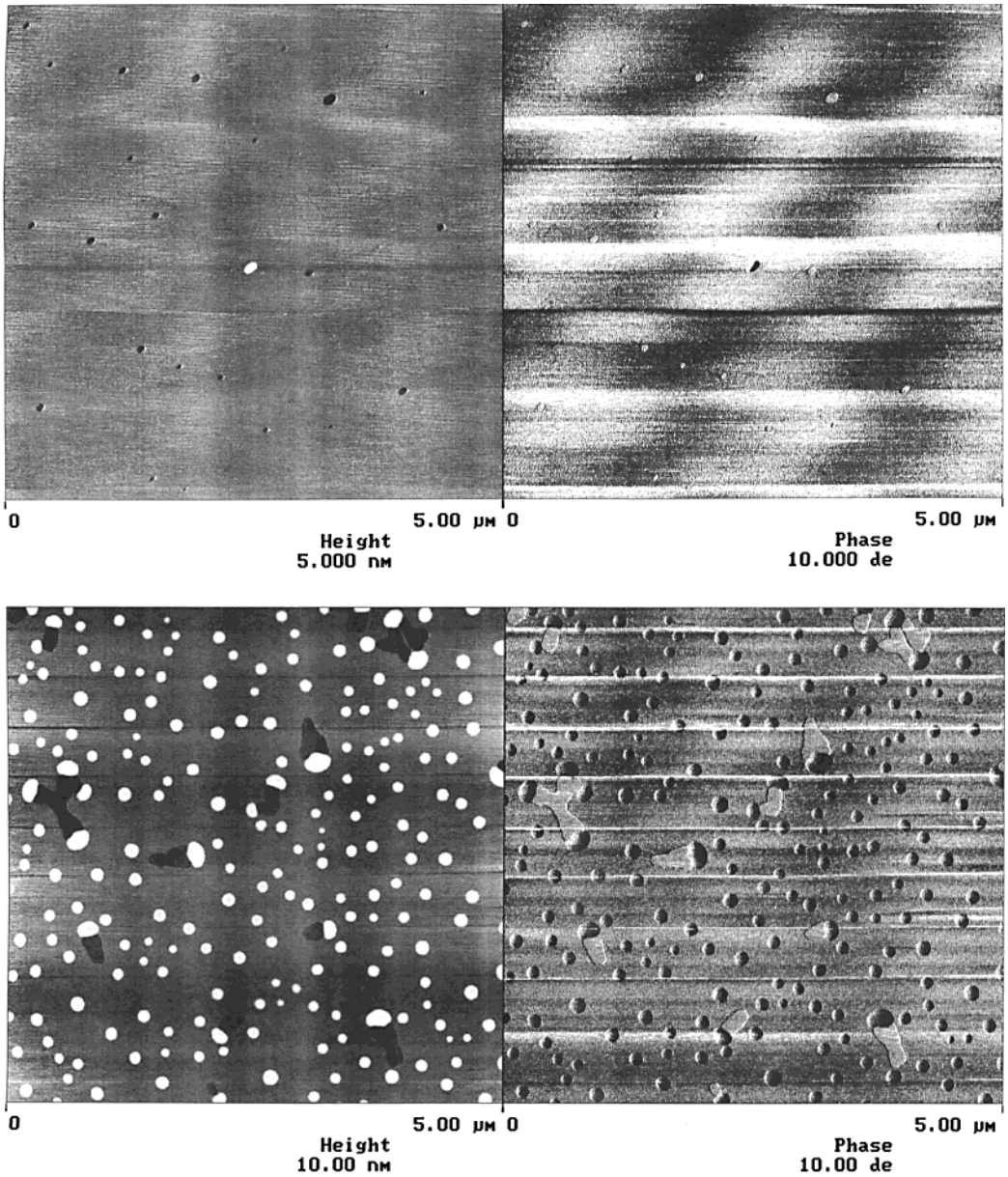


Figure 2. LB monolayer of monomer **11** on mica (a) as prepared and (b) 1 day after preparation. The height range from black to white is 10 nm with white being up.

attached "small" amphiphiles. Polymer **13** forms stable monolayers at the air/water interface which makes it reasonable to assume that it segregates lengthwise into homophilic domains with the short ethyleneoxy chains pointing into the subphase. The PPPs synthesized differ considerably in their hydrophilicity/hydrophobicity ratio, and many others with different ratios, size demands, branching patterns of the pendant groups, etc., will be accessible in the same manner. This will enable in the future to systematically investigate the surface and solution behavior of this class of novel polymeric amphiphiles.

Experimental Section

Compounds **3**,[10] **9a**,[11] and **12**[10] were prepared according to literature procedures. The catalyst precursor $Pd[P(p\text{-tolyl})_3]_3$[12] was prepared according to literature and stored no longer than 3 days in a high-quality glovebox. All the chemicals were purchased from Aldrich or Acros and used without further purification. Solvents were dried according to standard procedures. All reactions were carried out under nitrogen. NMR spectra of monomers and polymers were recorded on a Bruker AM 500 and all others on a Bruker AM 270 spectrometer. The molecular weight determinations were done using a Thermo Separation Products setup with three DVB−mixed (DVB = divinylbenzene) bead columns, a H520B viscosimeter detector, and a Wyatt Dawn DSP laser photometer, coupled with an Optilab 903 interferometric refractometer.

General Procedure for Reduction of Carboxylic Ester to Alcohol with $LiAlH_4$. A suspension of $LiAlH_4$ in THF was stirred for 2 h, and a solution of ester was then added dropwise. After the addition the mixture was stirred at room temperature overnight. A concentrated aqueous solution of NH_4Cl was added carefully to quench the reaction. The mixture was filtrated and the solid washed with THF until no more product could be detected. The combined solution was dried over Na_2SO_4 and evaporated to dryness. The crude product was purified as outlined.

General Procedure for Reduction of Carboxylic Ester to Alcohol with $LiBH_4$. $LiBH_4$ (4.5 equiv) in THF was refluxed for 1 h and then cooled to room temperature, and a solution of the ester (1.0 equiv) in THF was added dropwise. The mixture was refluxed for a further 8 h. THF was evaporated to dryness, and the residue acidified with dilute

HCl and extracted three times with CH_2Cl_2. The combined organic phase was dried over $MgSO_4$ and filtered through a short silica gel column.

General Procedure for Conversion of Benzylic Alcohol to Its Corresponding Bromide. To a stirred solution of alcohol and CBr_4 in minimum THF was added a solution of PPh_3 in THF at 0 °C. After addition the mixture was allowed to reach room temperature and stirred for 2 h. Addition of water quenched the reaction, and the mixture was extracted three times with CH_2Cl_2. The combined organic layer was dried over $MgSO_4$ and evaporated to dryness. The crude product was purified by silica gel column chromatography.

General Procedure for Ether Synthesis Using Phenol and Benzylic Bromide. A mixture of phenol, benzylic bromide, K_2CO_3, 18-crown-6, and acetone was refluxed for 24 h. The solvent is evaporated to dryness and the residue partitioned between water and CH_2Cl_2. The organic layer was separated, the aqueous layer extracted with CH_2Cl_2, and the combined organic layer dried over $MgSO_4$ and evaporated to dryness. (For **6b**: before drying, the combined organic phase was washed three times with aqueous solution of KBH_4, quickly acidified with dilute HCl, and washed with water.) The crude product was purified by silica gel chromatagraphy. The higher molecular weight compounds were freeze-dried after column separation.

General Procedure for Suzuki Polycondensation (SPC). A mixture of amphiphilic macromoner, 1,4-bezenediboronic acid propanediol ester, $NaHCO_3$, H_2O, and THF was carefully degassed before Pd[P(*p*-tolyl)$_3$]$_3$ was added. The mixture was stirred and refluxed for 3 or 7 days. CH_2Cl_2 (200 mL) was then added, and the organic layer was separated and dried over $MgSO_4$. After removal of the solvent, the residue was then dissolved in a minimum of CH_2Cl_2 (10 mL) and the solution dropped into ether (300 mL). The formed precipate was recovered by centrifugation, taken up in benzene, and freeze-dried.

2,5-Dibromo-4-methylbenzoic Acid (1b) A mixture of **1a** (187.5 g, 0.71 mol), nitric acid (65%, 800 mL), and water (550 mL) was heated and stirred at 100 °C for 7 days. The mixture was cooled to room temperature, and the solid was obtained by filtration and washed with water. The solid was dissolved in aqueous KOH solution (800 mL, 2 M), and this solution was washed with ether (2 × 200 mL) and gradually acidified with concentrated hydrochloric acid. The resulting precipitate was obtained by filtration, recrystallized from methanol, and dried under high vacuum. Yield of **1b**: 171 g (82%). The product, which can be used for next steps, contains traces of 2,5-dibromo-1,4-benzenedicarboxylic acid as impurities. Pure material can be obtained by silica gel column chromatography using ethyl acetate/hexane/methanol (1:1:0.1) as eluent. Anal. Calcd for $C_8H_6Br_2O_2$ (293.94): C, 32.69; H, 2.06. Found: C, 32.56; H, 1.86. ^{1}H NMR (270 MHz, DMSO-d_6): 2.30 (s, 3H), 7.66 (s, 1H), 7.89 (S, 1H). ^{13}C NMR (68 MHz, DMSO-d_6): 22.0, 119.5, 123.0, 132.1, 134.0, 135.9, 142.7, 165.7.

Methyl 2,5-Dibromo-4-methylbenzoate (1c). A mixture of **1b** (70 g, 0.24 mol), methanol (250 mL), and concentrated H_2SO_4 (10 mL) was refluxed for 6 h. Methanol was removed by distillation, and the residue was partitioned between ether and water. The organic phase was separated off and the aqueous one extracted with ether. The combined organic layer was washed with aqueous NaOH solution, water, and saturated NaCl solution, dried over $MgSO_4$, and evaporated to dryness. The crude product was used for subsequent reactions without further purification. Pure **1c** was obtained by silica gel chromatography eluting with hexane/ethyl acetate (14:1). Yield 64 g (87%). Anal. Calcd for $C_9H_8Br_2O_2$ (307.97): C, 35.10; H, 2.62. Found: C, 34.89; H, 2.51. ^{1}H NMR (270 MHz, $CDCl_3$): 2.38 (s, 3H), 3.90 (s, 3H), 7.55 (s, 1H), 8.01 (s, 1H). ^{13}C NMR (68 MHz, $CDCl_3$): 22.6, 52.5, 120.5, 123.3, 130.2, 135.0, 136.1, 143.4, 164.9.

Methyl 4-Bromomethyl-2,5-dibromobenzoate (1d). A solution of **1c** (55.7 g, 0.18 mol) and bromine (28.9 g, 0.18 mol) in 500 mL of CH_2Cl_2 was stirred and irradiated with UV light at 15−20 °C until the red color disappeared. Water was added, and the organic layer was separated and dried over $MgSO_4$ and evaporated to dryness. Pure **1d** was obtained by recrystallization from hexane/ethyl acetate (13:1) in 46 g (66%) yield. Anal. Calcd for $C_9H_7Br_3O_2$ (386.86): C, 27.94; H, 1.82. Found: C, 27.91; H, 1.82. ^{1}H NMR (270 MHz, $CDCl_3$): 3.96 (s, 3H), 4.50 (s, 2H), 7.72 (s, 1H), 8.00 (s, 1H). ^{13}C NMR (68 MHz, $CDCl_3$): 31.0, 52.8, 120.9, 122.7, 132.9, 135.8, 136.5, 141.7, 164.6.

Methyl 4-(4-Hydroxyphenoxy)methyl-2,5-dibromobenzoate (1e). A mixture of **1d** (15 g, 38.8 mmol), hydroquinone (44 g, 400 mmol), K_2CO_3 (11 g, 80 mmol), 18-crown-6 (10 mg), and acetone (350 mL) was heated to reflux for 24 h. Acetone was removed by distillation, the residue dispersed into water, and the crude product obtained by filtration and drying under high vacuum. Subsequent filtration of crude product through a short silica gel column using CH_2Cl_2/ether (1.5:1) as eluent followed by recrystallization from acetone gave pure **1e** as a white solid. Yield: 12.5 g (78%). Anal. Calcd for $C_{15}H_{12}Br_2O_4$ (416.06): C, 43.30; H, 2.91. Found: C, 43.01; H, 2.90. ^{1}H NMR (270 MHz, DMSO-d_6): 3.85 (s, 3H), 5.01 (s, 2H), 6.77 (AB system, 4H), 7.85 (s, 1H), 8.02 (s, 1H), 9.01 (s, 1H). ^{13}C NMR (68 MHz, DMSO-d_6): 52.8, 68.7, 115.8, 119.4, 120.9, 132.8, 134.1, 141.3, 141.6, 150.5, 151.9, 164.5.

Methyl 3,5-Bis[2-(2-methoxyethoxy)ethoxy]benzoate (4a). A mixture of methyl 3,5-dihydroxybenzoate **2** (23.2 g, 0.14 mol), 2-(2-methoxyethoxy)ethyl methyl sulfate **3** (66.1 g, 0.29 mol), K_2CO_3 (41.4 g, 0.30 mol), and DMF (1500 mL) was heated at 90 °C for 48 h. The mixture was allowed to cool to room temperature, and the solid was removed by filtration and washed thoroughly with acetone. The combined filtrate was evaporated to dryness, and the crude product was purified by silica gel column chromatography eluting with CH_2Cl_2 increasing to CH_2Cl_2/ether (4:1) to give pure **4a** as slightly yellow oil. Yield 32.2 g (62%). Anal. Calcd for $C_{18}H_{28}O_8$ (372.41): C, 58.05; H, 7.58. Found: C, 56.33; H, 7.09. ^{1}H NMR (270 MHz, $CDCl_3$): 3.32 (s, 6H), 3.50 (t, 4H), 3.63 (t, 4H), 3.79 (t, 4H), 3.81 (s, 3H), 4.09 (t, 4H), 6.63 (s, 1H), 7.10 (s, 2H). ^{13}C NMR (68 MHz, $CDCl_3$): 52.0, 58.9, 67.5, 69.4, 70.6, 71.7, 106.7, 107.9, 131.7, 159.6, 166.5.

3,5-Bis[2-(2-methoxyethoxy)ethoxy]benzyl Alcohol (4b). **4a** (20.0 g, 53.7 mmol), $LiAlH_4$ (2.7 g, 70 mmol), THF (200 mL). **4b** was obtained after drying under high vacuum as colorless oil, which was used without further purification. Yield 15.9 g (86%). ^{1}H NMR (270 MHz, $CDCl_3$): 3.3 (s, 6H), 3.5 (t, 4H), 3.7 (t, 4H), 3.8 (t, 4H), 4.1 (t, 4H), 4.6 (s, 2H), 6.3 (s, 1H), 6.5 (s, 2H). ^{13}C NMR (68 MHz, $CDCl_3$): 58.9, 65.0, 67.4, 69.6, 70.6, 71.8, 100.7, 105.4, 143.4, 159.9.

3,5-Bis[2-(2-methoxyethoxy)ethoxy]benzyl Bromide (4c). **4b** (6.6 g, 19.2 mmol), CBr_4 (8.3 g, 24.9 mmol), PPh_3 (6.5 g, 24.9 mmol), THF (20 mL). Eluent CH_2Cl_2 increasing to CH_2Cl_2/ether (2.5:1). Pure **4c** was obtained as colorless oil. Yield 6.0 g (76%). ^{1}H NMR (270 MHz, $CDCl_3$): 3.36 (s, 6H), 3.53 (t, 4H), 3.68 (t, 4H), 3.81 (t, 4H), 4.08 (t, 4H), 4.38 (s, 2H), 6.39 (s, 1H), 6.52 (s, 2H). ^{13}C NMR (68 MHz, $CDCl_3$): 33.5, 59.0, 67.5, 69.6, 70.7, 71.9, 101.7, 107.8, 139.5, 159.9.

Methyl 3,5-Bis{3,5-bis[2-(2-methoxyethoxy)ethoxy]-benzyloxy}benzoate (5a). **4c** (2.62 g, 6.44 mmol), compound **2** (0.53 g, 3.12 mmol), K_2CO_3 (1.5 g, 11 mmol), acetone (200 mL). Eluent CH_2Cl_2/ether (2.5:1) increasing to CH_2Cl_2/ether (1.5:1). Yield 2.5 g of **5a** as colorless oil (99%). Anal. Calcd for $C_{42}H_{60}O_{16}$ (820.92): C, 61.45; H, 7.37. Found: C, 61.05; H, 6.84. ^{1}H NMR (270 MHz, $CDCl_3$): 3.35 (s, 12H), 3.54 (t, 8H), 3.68 (t, 8H), 3.81 (t, 8H), 3.88 (s, 3H), 4.08 (t, 8H), 4.95 (s, 4H), 6.40 (s, 2H), 6.57 (s, 4H), 6.75 (s, 1H), 7.23 (s, 2H). ^{13}C NMR (68 MHz, $CDCl_3$): 52.2, 59.0, 67.5, 69.6, 70.1, 70.7, 71.9, 101.2, 106.1, 107.2, 108.3, 132.0, 138.7, 159.6, 160.1, 166.7.

3,5-Bis{3,5-bis[2-(2-methoxyethoxy)ethoxy]benzyloxy}-benzyl Alcohol (5b). **5a** (2.5 g, 3.11 mmol), $LiAlH_4$ (0.15 g, 4.00 mmol), THF (100 mL). **5b** was obtained after drying under high vacuum as colorless oil, which was used without further purification. Yield 2.18 g (88%). ^{1}H NMR (270 MHz, $CDCl_3$): 3.36 (s, 12H), 3.52 (t, 8H), 3.68 (t, 8H), 3.80 (t, 8H), 4.08 (t, 8H), 4.60 (s, 2H), 4.94 (s, 4H), 6.41 (s, 2H), 6.46 (s, 2H), 6.55 (s, 4H), 6.63 (s, 1H). ^{13}C NMR (68 MHz, $CDCl_3$): 59.0, 65.1, 67.4, 69.6, 69.8, 70.7, 71.9, 101.1, 101.3, 105.7, 106.0, 139.1, 143.5, 160.0.

3,5-Bis{3,5-bis[2-(2-methoxyethoxy)ethoxy]benzyloxy}-benzyl Bromide (5c). **5b** (10.5 g, 13.3 mmol), CBr_4 (8.8 g, 26.5 mmol), PPh_3 (7.0 g, 26.5 mmol). Eluent CH_2Cl_2 increasing to CH_2Cl_2/ether (65:35). Repeat column separation eluting with CH_2Cl_2/ether (65:35) gave pure **5c** as colorless oil. Yield 6.9 g (61%). Anal. Calcd for $C_{41}H_{59}O_{14}Br$ (855.81): C, 57.54; H, 6.95. Found: C, 57.37; H, 6.70. ^{1}H NMR (500 MHz, $CDCl_3$): 3.35 (s, 12H), 3.55 (t, 8H), 3.80 (t, 8H), 4.08 (t, 8H), 4.36 (s, 2H), 4.92 (s, 4H), 6.42 (s, 2H), 6.48 (s, 1H), 6.55 (s, 4H), 6.58 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): 33.6, 59.1, 67.4, 69.6, 69.9, 70.7, 71.9, 101.1, 102.1, 106.0, 108.0, 138.8, 139.7, 159.9, 160.0.

4-Dodecyloxyphenol (6). A mixture of hydroquinone (118.8 g, 1.08 mol), dodecyl bromide (44.8 g, 0.28 mmol), K_2CO_3 (74.5, 0.54 mol), and cyclohexanone (300 mL) was refluxed for 24 h. The solvent was removed in a vacuum, and the residue was partitioned between water and CH_2Cl_2. The organic layer was separated, and the aqueous one was extracted with CH_2Cl_2. The combined organic layer was washed successively with water, aqueous KBH_4 solution, dilute HCl solution, and saturated NaCl solution, dried over Na_2SO_4, and evaporated to dryness. Recrystallization from ethanol gave **6** as a colorless crystals. Yield 35.5 g (71%). ^{1}H NMR (270 MHz, $CDCl_3$): 0.92 (t, 3H), 1.28−1.40 (m, 18H), 1.79 (p, 2H), 3.88 (t, 2H), 4.78 (broad, 1H), 6.78 (AB system, 4H). ^{13}C NMR (68 MHz, $CDCl_3$): 14.1, 22.7, 26.0, 29.3, 29.6, 31.9, 68.8, 115.6, 116.0, 149.3, 153.2.

Methyl2,5-Dibromo-4-[4-(dodecyloxy)phenoxymethyl]-benzoate (7a). **1d** (3.74 g, 13.44 mmol), **6** (4. 00 g, 10.3 mmol), K_2CO_3 (8.56 g, 62.0 mmol), 18-crown-6 (10 mg), acetone (300 mL). Chromatographical separation through silica gel column using hexane/ethyl acetate (10:1) as eluent, and recrystallization from ethanol gave **7a** as colorless solid. Yield 5.2 g (85%). ^{1}H NMR (270 MHz, $CDCl_3$): 0.92 (t, 3H), 1.20−1.32 (m, 18H), 1.72 (p, 2H), 3.88 (t, 2H), 3.92 (s, 3H), 5.00 (s, 2H), 6.80 (AB system, 4H), 7.88 (s, 1H), 8.00 (s, 1H). ^{13}C NMR (68 MHz, $CDCl_3$): 14.1, 22.7, 26.0, 29.3, 29.6, 31.9, 52.7, 68.6, 69.2, 115.5, 115.9, 119.9, 121.1, 132.0, 133.9, 135.0, 141.8, 151.9, 154.1, 165.0.

2,5-Dibromo-4-[4-(dodecyloxy)phenoxymethyl]benzyl Alcohol (7b). **7a** (5.2 g, 8.8 mmol), $LiBH_4$ (4.4 g, 37.0 mmol), THF (300 mL). Chromatographical separation through silica gel column using CH_2Cl_2 as eluent gave **7b** as colorless solid. Yield 4.2 g (86%). Anal. Calcd for $C_{26}H_{36}Br_2O_3$ (556.38): C, 56.13; H, 6.52. Found: C, 56.23; H, 6.36. ^{1}H NMR (270 MHz, $CDCl_3$): 0.86 (t, 3H), 1.25−1.42 (m, 18H), 1.74 (p, 2H), 3.88 (t, 2H), 4.67 (s, 2H), 4.99 (s, 2H), 6.85 (AB system, 4H), 7.68 (s, 1H), 7.71 (s, 1H). ^{13}C NMR (68 MHz, $CDCl_3$): 14.1, 22.7, 26.0, 29.3, 29.6, 31.9, 64.1, 68.6, 69.3, 115.4, 115.8, 120.9, 121.1, 132.1, 132.2, 137.5, 140.7, 152.1, 153.8.

2,5-Dibromo-4-(4-dodecyloxyphenoxymethyl)benzyl Bromide (7c). **7b** (4.7 g, 8.5 mmol), CBr_4 (5.6 g, 16.9 mmol), PPh_3 (4.4 g, 16.9 mmol), THF (50 mL). Chromatographical separation through silica gel column eluting with CH_2Cl_2 gave **7c** as colorless solid. Yield 3.9 g (74%). Anal. Calcd for $C_{26}H_{35}Br_3O_2$ (619.27): C, 50.43; H, 5.70. Found: C, 50.41; H, 5.54. ^{1}H NMR (270 MHz, $CDCl_3$): 0.86 (t, 3H), 1.25−1.43 (m, 18H), 1.74 (p, 2H), 3.89 (t, 2H), 4.52 (s, 2H), 4.98 (s, 2H), 6.86 (AB system, 4H), 7.63 (s, 1H), 7.77 (s, 1H). ^{13}C NMR (68 MHz, $CDCl_3$): 14.1, 22.7, 26.0, 29.3, 29.6, 31.9, 68.6, 69.2, 115.4, 115.8, 120.6, 123.5, 132.9, 134.5, 137.8, 139.0, 152.0, 153.9.

4-[2,5-Dibromo-4-(4-dodecyloxyphenoxymethyl)benzyloxy]phenol (7d). **7c** (2.0 g, 3.2 mmol), hydroquinone (3.6 g, 32.3 mmol), K_2CO_3 (2.2 g, 16.2 mmol), 18-crown-6 (10 mg), acetone (250 mL). Chromatographical separation through silica gel column eluting with CH_2Cl_2 gave **7d** as colorless solid. Yield 1.3 g (62%). Anal. Calcd for $C_{32}H_{40}O_4Br_2$ (648.47): C, 59.27; H, 6.22. Found: C, 59.25; H, 6.16. ^{1}H NMR (270 MHz, $CDCl_3$): 0.86 (t, 3H), 1.26−1.42 (m, 18H), 1.74 (p, 2H), 3.88 (t, 2H), 4.72 (s, 1H), 5.0 (s, 4H), 6.76−6.91 (two sets of AB system, 8H), 7.75 (s, 2H). ^{13}C NMR (68 MHz, $CDCl_3$): 14.1, 22.7, 26.0, 29.3, 29.4, 29.6, 31.9, 68.6, 69.4, 115.4, 115.8, 116.0, 116.1, 116.1, 118.6, 120.9, 132.2, 137.6, 137.7, 150.0, 152.1, 152.3, 153.8.

4-{3,5-Bis{3,5-bis[3,5-bis(benzyloxy)benzyloxy]benzyloxy}benzyloxy}phenol (9b). **9a** (4.0 g, 2.4 mmol), hydroquinone (10.0 g, 90.8 mmol), K_2CO_3 (9.0 g, 65.0 mmol). For **6b** yield 2.95 g (72%). Anal. Calcd for $C_{111}H_{96}O_{16}$ (1685.96): C, 79.07; H, 5.74. Found: C, 78.54; H, 5.67. ^{1}H NMR (270 MHz, $CDCl_3$): 4.65 (s, 1H), 4.88 (s, 2H), 4.93 (s, 12H), 5.01 (s, 16H), 6.55−6.82 (four sets of signals, 25H), 7.42−7.27 (m, 40). ^{13}C NMR (68 MHz, $CDCl_3$): 69.9, 70.1, 70.5, 101.6, 106.4, 116.0, 127.5, 128.0, 128.5, 136.7, 139.2, 140.0, 149.7, 153.0, 160.0, 160.1.

Methyl 2,5-Dibromo-4-{4-{2-{2-[2-(2-methoxyethoxy)-ethoxy]ethoxy}ethoxy}ethoxy} phenoxymethylbenzoate (10a). A mixture of **1e** (4.7 g, 11.4 mmol), 2-{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}ethoxy}ethyl tolyl sulfate (4.9 g, 12.1 mmol), K_2CO_3 (1.8 g, 13 mmol), 18-crown-6 (10 mg), and KI (2.16 g, 13 mmol) in DMF (300 mL) was heated to 90 °C for 24 h. The reaction mixture was filtrated, the solid washed thoroughly with acetone, and the combined filtrate evaporated to dryness under reduced pressure. The crude material was subjected two times to silica gel column separation with CH_2Cl_2/ether as eluent to give **9a** as colorless oil. ^{1}H NMR (270 MHz, $CDCl_3$): 3.33 (s, 3H), 3.50 (t, 2H), 3.65 (m, 14H), 3.80 (t, 2H), 3.91 (s, 3H), 4.05 (t, 2H), 5.00 (s, 2H), 6,85 (AB, 4H), 7.84 (s, 1H), 7.96 (s, 1H). ^{13}C NMR (68 MHz, $CDCl_3$): 52.6, 58.9, 67.9, 69.0, 69.7, 70.4, 70.5, 70.7, 71.8, 72.6, 74.2, 115.6, 115.7, 119.8, 121.0, 131.9, 133.8, 134.7, 134.9, 141.7, 152.1, 153.6, 164.9.

2,5-Dibromo-4-{4-{2-{2-[2-(2-methoxyethoxy)ethoxy]-ethoxy}ethoxy}ethoxy} phenoxymethylbenzyl Alcohol (10b). $LiBH_4$ (0.455 g, 20.9 mmol), **10a** (3.0 g, 4.6 mmol), and THF (150 mL) were used. Filtration of the crude product through a short column gave **9b** as colorless oil. Yield 2.7 g (94%). ^{1}H NMR (270 MHz, $CDCl_3$): 3.33 (s, 3H), 3.52 (t, 2H), 3.65 (m, 14H), 3.80 (t, 2H), 4.04 (t, 2H), 4.65 (s, 2H), 4,96 (s, 2H), 6.85 (AB, 4H), 7.65 (s, 1H), 7.68 (s, 1H). ^{13}C NMR (68 MHz, $CDCl_3$): 58.9, 63.7, 67.9, 69.2, 69.7, 70.5, 71.8, 115.6, 115.7, 120.7, 120.9, 131.8, 132.0, 137.1, 141.1, 152.3, 153.6.

2,5-Dibromo-4-{4-{2-{2-[2-(2-methoxyethoxy)ethoxy]-ethoxy}ethoxy}ethoxy} phenoxymethylbenzyl Bromide (10c). To a solution of CBr_4 (2.88 g, 8.7 mmol), **10b** (2.70 g, 4.3 mmol) in 15 mL of THF was dropped a solution of PPh_3 (2.28 g, 8.7 mmol) in THF (15 mL) at 0 °C. The mixture was then stirred at room temperature for 90 min and water added. The mixture was extracted three times with CH_2Cl_2, and the combined organic layer was dried over $MgSO_4$ and evaporated to dryness. The crude product was purified by silica gel column chromatography eluting with CH_2Cl_2/ether (2:1) to give **9c** as colorless oil. Yield 2.5 g (84%). Anal. Calcd for $C_{25}H_{33}Br_3O_7$ (685.24): C, 43.82; H, 4.85. Found: C, 43.95; H, 4.91. ^{1}H NMR (270 MHz, $CDCl_3$): 3.34 (s, 3H), 3.52 (t, 2H), 3.65 (m, 14H), 3.80 (t, 2H), 4.06 (t, 2H), 4.50 (s, 2H), 4.97 (s, 2H), 6,85 (AB, 4H), 7.61 (s, 1H), 7.75 (s, 1H). ^{13}C NMR (68 MHz, $CDCl_3$): 31.8, 59.0, 68.0, 69.2, 69.8, 70.5, 70.6, 70.8, 71.9, 115.7, 115.8, 120.6, 123.5, 132.9, 134.5, 137.8, 138.9, 152.3, 153.6.

1-{4-{3,5-Bis{3,5-bis[3,5-bis(benzyloxy)benzyloxy]-benzyloxy}benzyloxy}phenoxymethyl}-2,5-dibromo-4-{4-{2-{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}ethoxy}ethoxy}-phenoxymethylbenzene (11). **10c** (1.65 g, 2.4 mmol), **9b** (4.06 g, 2.4 mmol), K_2CO_3 (1.2 g, 8.7 mmol), acetone (250 mL). Eluent: CH_2Cl_2/ether (2:1). Yield 3.92 g (71%). Anal. Calcd for $C_{136}H_{128}Br_2O_{23}$ (2290.29): C, 71.32; H, 5.63. Found: C, 71.19; H, 5.92. ^{1}H NMR (500 MHz, $CDCl_3$): 3.36 (s, 3H), 3.54 (t, 2H), 3.65 (m, 12H), 3.73 (t, 2H), 3.85 (t, 2H), 4.08 (t, 2H), 4.93−5.01 (four sets of peaks, 34H), 6.55 (m, 7H), 6.66 (m, 14H), 6.88 (m, 8H), 7.27−7.40 (m, 40H), 7.76 (s, 1H), 7.77 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): 59.01, 67.90, 69.20, 69.76, 69.89, 69.99, 70.39, 70.45, 70.51, 70.54, 70.73, 71.85, 101.46, 106.26, 115.56, 115.73, 115.79, 120.88, 120.92, 127.53, 127.97, 128.54, 132.15, 136.65, 137.57, 137.60, 139.10, 139.14, 139.61, 152.36, 152.43, 153.30, 153.43, 159.96, 160.06.

1-{4-{3,5-Bis{3,5-bis[2-(2-methoxyethoxy)ethoxy]-benzyloxy}benzyloxy}phenoxymethyl}-2,5-dibromo-4-(4-dodecyloxyphenoxymethyl)benzene (8). **7d** (1.90 g, 2.9 mmol), **5c** (2.50 g, 2.9 mmol), K_2CO_3 (2 g, 14.0 mmol), acetone

(200 mL). Eluent: CH_2Cl_2/ether (2:1) increasing to 1.5:1. Yield 3.3 g (79%). Anal. Calcd for $C_{73}H_{98}O_{18}Br_2$ (1423.37): C, 61.60; H, 6.94. Found: C, 61.63; H, 6.83. ^{1}H NMR (500 MHz, $CDCl_3$): 0.86 (t, 3H), 1.24 (m, 16H), 1.42 (p, 2), 1.73 (p, 2H), 3.37 (s, 12H), 3.55 (t, 8H), 3.69 (t, 8H), 3.82 (t, 8H), 3.88 (t, 2H), 4.10 (t, 8H), 4.94−5.00 (four sets of signals incorporated to two peaks, 10H), 6.43 (t, 2H), 6.51 (t, 1H), 6.56 (d, 4H), 6.62 (d, 2H), 6.80−6.89 (m, 8H), 7.76 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): 14.13, 22.66, 26.00, 29.30, 29.33, 29.38, 29.55, 29.57, 29.60, 29.62, 31.87, 59.09, 67.31, 68.45, 69.16, 69.21, 69.61, 69.83, 70.31, 70.66, 71.84, 100.93, 101.32, 105.92, 106.10, 115.29, 115.71, 115.74, 120.89, 132.12, 137.54, 137.64, 138.93, 139.50, 152.03, 152.38, 153.28, 153.76, 153.76, 159.94.

Poly{2-{4-{3,5-bis{3,5-bis[2-(2-methoxyethoxy)ethoxy]benzyloxy}benzyloxy}phenoxymethyl}-5-(4-dodecyloxyphenoxymethyl)biphen-4,4′-diyl} (**13**). **8** (815 mg, 0.57 mmol), **12** (141.4 mg, 0.58 mmol), $NaHCO_3$ (1.5 g), THF (15 mL), H_2O (10 mL), Pd[P(*p*-tolyl)$_3$]$_3$ (4.0 mg, 0.65 mol %). Yield: 0.73 g (95%). Anal. Calcd for $[C_{79}H_{102}O_{18}]_n$: C, 70.83; H, 7.67. Found: C, 70.15; H, 7.33. ^{1}H NMR (500 MHz, $CDCl_3$): 0.84 (broad, 3H), 1.22 (broad, 16H), 1.38 (broad, 2H), 1.70 (broad, 2H), 3.34 (broad, 12H), 3.52 (broad, 8H), 4.90 (broad, 10H), 6.41 (broad, 2H), 6.49 (broad, 1H), 6.54 (broad, 4H), 6.62 (broad, 2H), 6.71−6.90 (broad, 8H), 7.40−7.80 (broad, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): 14.11, 22.64, 26.01, 29.31, 29.57, 31.86, 59.02, 64.09, 67.33, 68.44, 69.59, 69.81, 70.63, 71.83, 100.97, 105.96, 106.23, 115.20, 115.81, 129.20, 138.98, 153.11, 159.95.

Poly{2-{4-{3,5-bis{3,5-bis[3,5-bis(benzyloxy)benzyloxy]bezyloxy}benzyloxy}phenoxymethyl}-5-{4-{2-{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}ethoxy}ethoxy}-phenoxymethylbiphen-4,4′-diyl} (**14**). **10** (808 mg, 0.35 mmol), **11** (87.2 mg, 0.34 mmol), THF (15 mL), H_2O (6 mL), Pd[P(*p*-tolyl)$_3$]$_3$ (2.3 mg, 0.65 mol %). Yield 706 mg (91%). Anal. Calcd for $[C_{142}H_{132}O_{23}]_n$: C, 77.29; H, 6.03. Found: C, 75.63; H, 5.91. ^{1}H NMR (500 MHz, $CDCl_3$): 3.33 (broad, 3H), 3.49 (broad, 2H), 3.59 (broad, 14H), 3.74 (broad, 2H), 3.98 (broad, 2H), 4.75−5.00 (broad, 34H), 6.47 (broad, 7H), 6.58 (broad, 14H), 6.74 (broad, 8H), 7.27−7.35 (broad, 40H), 7.48−7.64 (broad, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): 58.96, 67.81, 68.55, 69.77, 69.89, 70.74, 70.64, 71.81, 100.80, 101.42, 102.04, 105.61, 106.24, 106.90, 115.41, 115.57, 115.74, 126.88, 127.49, 127.90, 128.14, 128.48, 129.15, 131.42, 134.15, 136.66, 139.12, 139.59, 140.66, 152.87, 153.11, 159.91, 160.01.

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