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Synthesis and Structure of Cyclic Oligo(*p*-phenylene oxide)s, $-(C_6H_4O)_n-$ ($n = 6-10$)

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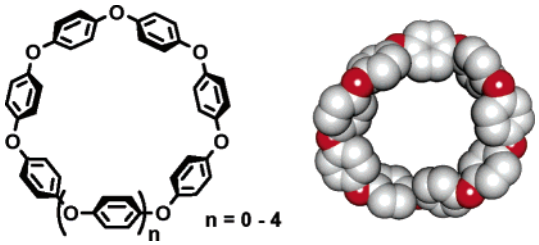
Received May 14, 2006



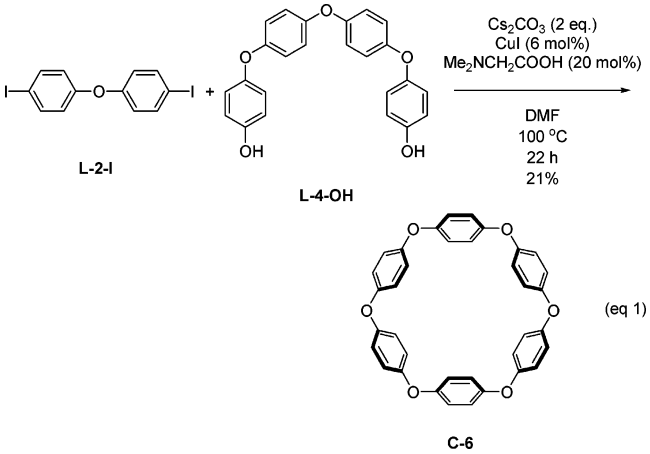
Stepwise growth of oligo(*p*-phenylene oxide)s and cyclization via the Ullmann coupling reaction by using CuI/*N*,*N*-dimethylglycine afforded cyclic oligo(*p*-phenylene oxide)s, $-(C_6H_4O)_n-$ ($n = 6-10$). The structure of the new cyclophanes was determined by X-ray crystallography, which revealed that they have planar or slightly bent structures with diameters of 1.0−1.5 nm.

Various cyclophanes composed of the aromatic groups attached to OH or OR groups have been investigated[1] partly because the electron-rich aromatic rings are able to form a complex with electron-deficient guest molecules such as C_{60}. Attractive interaction between hydroquinones and C_{60}, forming a 3:1 complex, was observed in the solid state.[2] Fully aromatic crown ethers are also expected to exhibit attractive interaction with electron-deficient molecules and to form a host−guest complex, although their synthetic examples are rare and the yield is very low.[3] Quite recently, Gibb reported templated synthesis of cyclic oligo(*m*-phenylene oxide)s.[4,5]

Although examples of cyclic oligo(*p*-phenylene sulfide)s are known,[6,7] there have been few reports on efficient synthesis of the cyclic oligo(*p*-phenylene oxide)s, $-(C_6H_4O)_n-$, with suitable ring size for the host−guest complexation. Vögtle conducted copper-catalyzed Ullmann coupling of 4-bromophenol and obtained a mixture of the cyclic oligo(*p*-phenylene oxide)s with $n = 5-9$.[8] Recently, Ma has reported that the Ullmann coupling reaction using CuI/*N*,*N*-dimethylglycine catalyst enabled coupling of phenols with aryl iodides under mild conditions.[9] Ullmann coupling catalyzed by Cu_2O in the presence of Cs_2CO_3 and K_3PO_4 (with aryl iodide and bromides, respectively) and *trans*-1,2-bis(2′-pyridylidenamino)cyclohexane has also been found by Taillefer.[10] Herein, we report application of these new Ullmann coupling reactions to selective synthesis of the cyclic oligo(*p*-phenylene oxide)s.

Scheme 1 shows two routes for synthesis of linear phenylene oxide tetramer terminated with two OH groups **L-4-OH**. Analogous penta(phenylene oxide), $HOC_6H_4O(C_6H_4O)_3C_6H_4$-OH, was prepared by Tashiro by using a similar Ullmann coupling reaction by using CuCl (80−150 mol %) at 80 °C.[11] A 2:1 coupling reaction of 4-methoxymethoxyphenol formed by protection of a hydroxy group of dihydroquinone[12] and 4,4′-dibromodiphenyl ether in the presence of CuI/*N*,*N*-dimethylglycine resulted in formation of a linear tetramer **L-4-OMOM** in 63% yield. Removal of the methoxymethyl group with HCl gives **L-4-OH** in 98% yield (Scheme 1, method A). Coupling of 4-methoxyphenol and 4,4′-diiododiphenyl ether, synthesized by the reaction of diphenyl ether with *N*-iodosuccinimide,[13] forms **L-4-OMe** in 86% yield. Subsequent demethylation by BBr_3 yields **L-4-OH** in 90% yield (Scheme 1, method B).

An equimolar reaction of **L-4-OH** with 4,4′-diiododiphenyl ether in the presence of the Cu reagent afforded the cyclic hexamer, **C-6** (eq 1). Table 1 summarizes the results of the cyclization. The reaction of 4,4′-diiododiphenyl ether with **L-4-OH** in dioxane for 168 h did not form the cyclic product (run 1),



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10.1021/jo0609982 CCC: $33.50
Published on Web 10/06/2006

SCHEME 1. Synthesis of L-4-OH

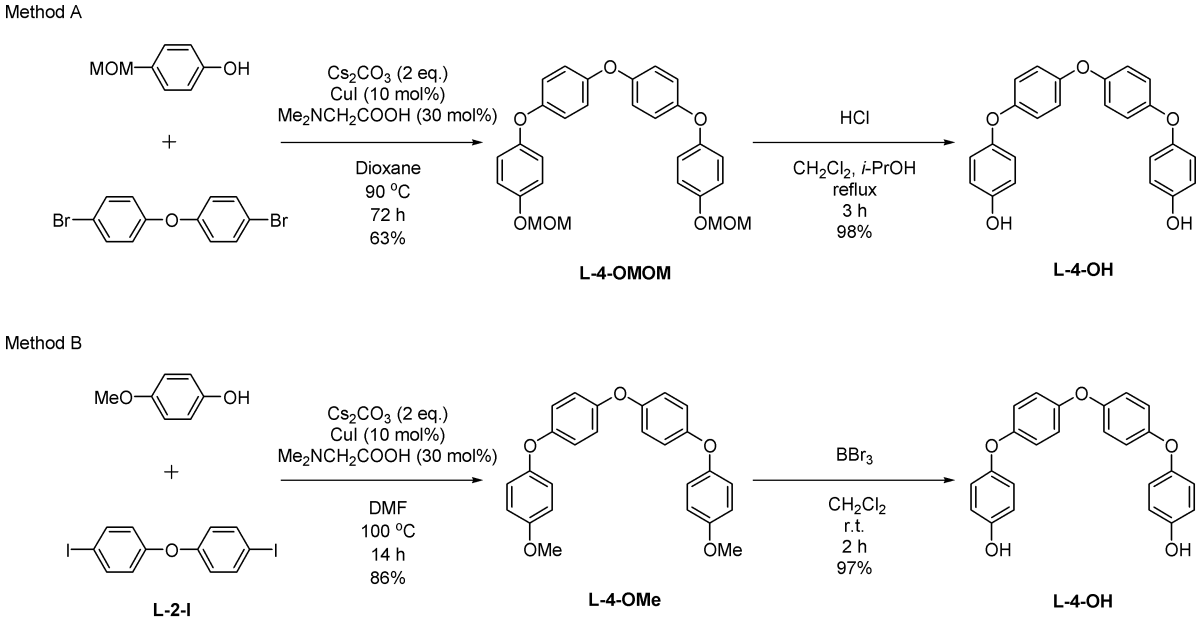


TABLE 1. Synthesis of Cyclic Oligo(*p*-phenylene oxide)s

	reactant[a]		reaction						
run	HO-Ar-OH	I-Ar′-I	catalyst[c]	solvent	HO-Ar-OH (mM)	*T* (°C)	time (h)	product[b]	
1	**L-4-OH**	**L-2-I**	A	dioxane	50	90	168	no reaction	
2	**L-4-OH**	**L-2-I**	A	DMF	25	100	22	**C-6**	(17)
3	**L-4-OH**	**L-2-I**	A	DMF	5	100	44	**C-6**	(8.1)
4	**L-4-OH**	**L-2-I**	A	DMSO	25	100	20	**C-6**	(11)
5	**L-4-OH**	**L-2-I**	B	DMF	25	110	64	**C-6**	(11)
6[d]	**L-4-OH**	**L-2-I**	A	$C_2H_2Cl_4$	30	100	148	no reaction	
7[d]	**L-4-OH**	**L-2-I**	A	DMF	25	100	36	no reaction	
8[e]	**L-4-OH**	**L-2-I**	A	DMF	25	100	36	**C-6**	(8.9)
9	**L-6-OH**	**L-1-I**	A	DMF	5	100	20	**C-7**	(19)
10	**L-6-OH**	**L-2-I**	A	DMF	5	100	20	**C-8**	(20)
11	**L-6-OH**	**L-3-I**	A	DMF	5	100	18	**C-9**	(27)
12	**L-6-OH**	**L-4-I**	A	DMF	5	100	16	**C-10**	(21)

[a] HO-Ar-OH (1.0 mmol) and I-Ar′-I (1.0 mmol) were used as the reactants. [b] Yields are in parentheses. [c] A: CuI (0.2 mmol), Me_2NCH_2COOH·HCl (0.6 mmol), Cs_2CO_3 (4.0 mmol). B: Cu_2O (0.05 mmol), *trans*-1,2-bis(2′-pyridylidenamino)cyclohexane (0.2 mmol), Cs_2CO_3 (4.0 mmol), MS3A (60 mg). [d] Me_4NBr was added. [e] Et_4NI was added.

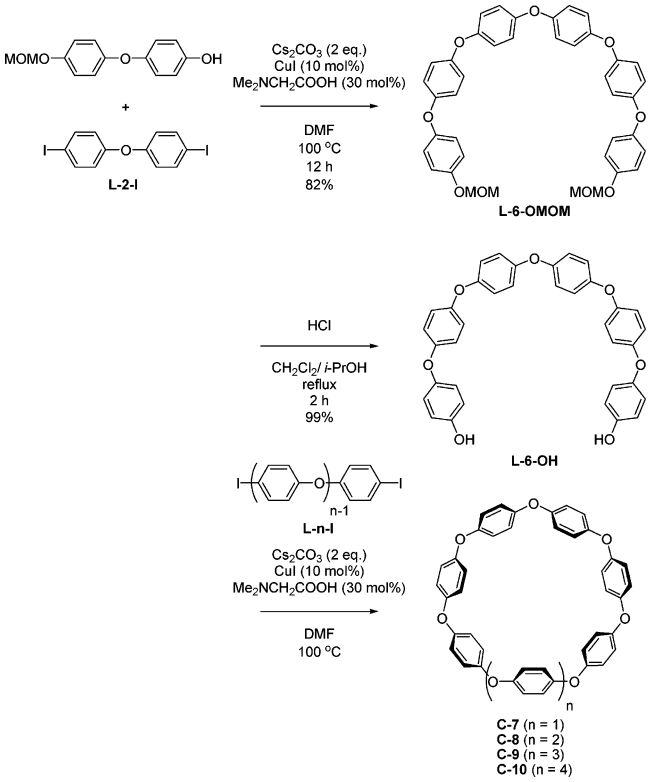
probably due to low solubility of **L-4-OH** in dioxane. The reaction with **L-4-OH** at 100 °C, 22 h, in a DMF solution (25 mM) proceeds more smoothly to give a mixture of the cyclic and linear oligo(*p*-phenylene oxide)s. After removal of DMF by evaporation, extraction from the residue with $CHCl_3$ afforded analytically pure **C-6** in 17% yield (run 2). The reaction with low concentration of **L-4-OH** (5 mM) and that in DMSO also produced **C-6** in 8.1% (runs 3 and 4). Analogous cyclization by condensation using Cu_2O/*trans*-1,2-bis(2′-pyridylidenamino)-cyclohexane produced the cyclic oligomer in 11% yield (run 5). Addition of quaternary ammonium salts, which may act as potential templates for the cyclization, did not improve yield of the desired product (runs 6−8).

Cyclic oligo(*p*-phenylene oxide)s with larger ring sizes were also synthesized. Linear hexamer **L-6-OH** was synthesized by the coupling of 4-hydroxy-4′-methoxymethoxydiphenyl ether with 4,4′-diiododiphenyl ether in the presence of CuI/*N*,*N*-dimethylglycine in DMF followed by removal of the MOM group by treatment with HCl. The reaction of **L-6-OH** with 1,4-diiodobenzene in the presence of the copper catalyst produced the cyclic heptamer, C-7, in 26% yield (run 9). **L-6-OH** underwent cyclizative coupling with **L-2-I**, **L-3-I**, and **L-4-I** to afford **C-8**, **C-9**, and **C-10** in the respective yields of 20, 27, and 21% after simple evaporation of DMF and extraction with $CHCl_3$ (runs 10−12).

The NMR and MS spectra of **C-6**−**C10** are consistent with the cyclic structure (Scheme 2). For example, the ^{1}H NMR spectrum of **C-9** shows one singlet signal at δ 6.96, which is assigned to the phenylene hydrogens. The $^{13}C\{^1H\}$ NMR spectrum of **C-9** shows signals at δ 119.8 and 153.1 due to CH and quaternary carbons, respectively. The FAB-MS spectrum of **C-9** shows a signal at 828.2348, which is in agreement with the calculated molecular weight (828.2359).

Recrystallization of the cyclic oligo(*p*-phenylene oxide)s from CH_2Cl_2/hexane or $CHCl_3$/hexane affords single crystals suitable for X-ray crystal structure analysis. ORTEP view of **C-6**−**C-9** is shown in Figure 1. The crystals contain CH_2Cl_2 or $CHCl_3$ molecules used in recrystallization. A Cl atom of the CH_2Cl_2 molecule exists at the center of the pore of **C-6**, while two molecules are positioned outside of the macrocycle. A $CHCl_3$ molecule is included within the bent macrocycle of **C-7**. **C-8** and **C-9** contain a $CHCl_3$ molecule inside of the pore. The **C-9** has an extra inside space, which is filled by a phenylene oxide unit of another **C-9** molecule. The neighboring phenylene planes

SCHEME 2. Synthesis of C-7−C-10



of **C-6** are situated almost perpendicularly, while the neighboring aromatic planes of **C-7**, **C-8**, and **C-9** are twisted with smaller angles. **C-6** and **C-8** have almost planar structure structures, whereas **C-7** and **C-9** have bent structures due to an even−odd effect. The $^{13}C\{^1H\}$ NMR spectra of **C-6**−**C-9**, however, show a single signal, indicating that the phenylene planes rotate faster than the NMR time scale in solution. The diameters of **C-6** and **C-9** are estimated as approximately 1.0 and 1.5 nm.

In summary, we succeeded in synthesizing cyclic hexa- to deca(*p*-phenylene oxide)s by Ullmann coupling using CuI/*N*,*N*-dimethylglycine. Structures of the cyclic hexa- to nona(*p*-phenylene oxide)s were determined by X-ray crystallography, which revealed that they have planar or slightly bent structures with diameters of 1.0−1.5 nm. The cyclic oligo(*p*-phenylene oxide)s, thus formed, will be used as modules in supramolecular chemistry.

Experimental Section

4-(Methoxymethoxy)phenol. To a 100-mL round-bottomed flask containing hydroquinone (4.0 g, 26 mmol), *N*,*N*-diisopropylethylamine (3.3 mL, 38 mmol), and acetonitrile (120 mL) was added methoxymethyl chloride (2.3 g, 28 mmol) slowly at 0 °C. The mixture was stirred at room temperature for 8 h, ethyl acetate was added, and the mixtrue was washed with water (3 times). The organic phase was dried over $MgSO_4$, volatiles were evaporated, and the residue was chromatographed on silica gel (ethyl acetate/hexane = 1:10) to obtain 4-(methoxymethoxy)phenol as a white solid (1.5 g, 9.9 mmol, 38% yield): ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 6.91 (d, 2H, J = 9.0 Hz), 6.73 (d, 2H, J = 9.0 Hz), 5.10 (s, 2H), 3.49 (s, 3H); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$, 25 °C) δ 151.2, 150.3, 118.0, 116.1, 95.5, and 55.9. 4-Hydroxy-4′-(methoxymethoxy)diphenyl ether was prepared similarly from 4,4′-dihydroxydiphenyl ether (38% yield): ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 7.63 (d, 2H, J = 9.0 Hz), 6.76 (d, 2H, J = 9.0 Hz), 5.10 (s, 2H), 3.49 (s, 3H); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$, 25 °C) δ 152.9, 152.7, 151.4, 120.9, 119.3, 117.7, 116.3, 95.2, and 56.0.

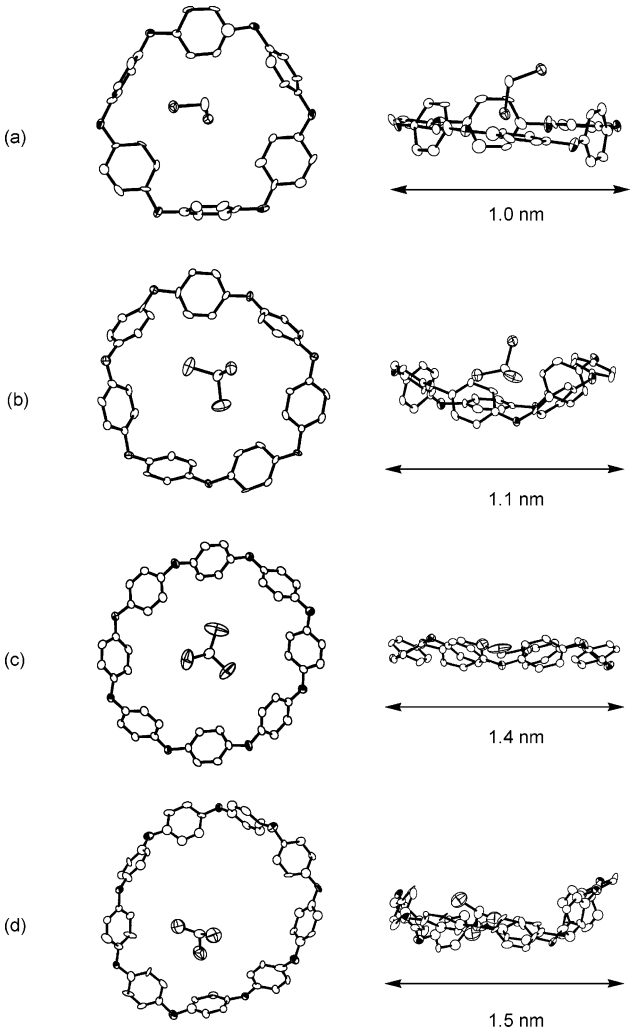


FIGURE 1. ORTEP views of cyclic oligo(*p*-phenylene oxide)s (a) **C-6**, (b) **C-7**, (c) **C-8**, and (d) **C-9** at the 30% ellipsoidal level. Hydrogen atoms are omitted for clarity.

4,4′-Diiododiphenyl Ether. To a 100-mL round-bottomed flask were added diphenyl ether (1.0 g, 5.9 mmol), *N*-iodosuccinimide (2.8 g, 12 mmol), acetonitrile (20 mL), and trifluoroacetic acid (1 drop), and the mixture was refluxed for 4 h. Chloroform was added, and the organic phase was washed with $Na_2S_2O_3$ aq (1 time) and water (2 times), which was dried over $MgSO_4$. The volatiles were evaporated, and the residue was recrystallized from chloroform/hexane to obtain 4,4′-diiododiphenyl ether as a white solid (2.2 g, 5.2 mmol, 88% yield): ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 7.63 (d, 2H, J = 9.0 Hz), and 6.76 (d, 2H, J = 9.0 Hz). 4,4′-Bis(4-iodophenoxy)benzene (**L-3-I**) (90% yield) and 4,4′-bis(4-iodophenoxy)diphenyl ether (**L-4-I**) (90% yield) were prepared similarly. **L-3-I**: ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 7.61 (d, 4H, J = 9.0 Hz), 6.99 (s, 4H), and 6.76 (d, 4H, J = 9.0 Hz); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$, 25 °C) δ 187.0, 157.7, 152.4 138.7 120.7, and 120.4. **L-4-I**: ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 7.60 (d, 4H, J = 9.0 Hz), 6.99 (s, 8H), and 6.75 (d, 4H, J = 9.0 Hz).

4,4′-Bis[4-(methoxymethoxy)phenoxy]diphenyl Ether. To a 100-mL round-bottomed flask were added 4-(methoxymethox)-phenol (0.65 g, 3 mmol), 4,4′-dibromodiphenyl ether (0.33 g, 1 mmol), CuI (38 mg, 0.2 mmol), *N*,*N*-dimethylglycine hydrochloride (84 mg, 0.6 mmol), Cs_2CO_3 (1.4 g, 4 mmol), and 1,4-dioxane (4 mL), and the mixture was stirred at 90 °C for 72 h. Ethyl acetate was added, and the organic phase was washed three times with water. After the phase was dried over $MgSO_4$, volatiles were evaporated, and the residue was chromatographed on silica gel

(ethyl acetate/hexane = 1:10) to obtain 4,4′-bis[4-(methoxymethoxy)phenoxy]diphenyl ether as a white solid (0.9 g, 1.9 mmol, 63% yield): ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 7.03−6.92 (m, 16H), 5.14 (s, 4H), 3.49 (s, 6H); $^{13}C\{^1H\}$ NMR (75.5 MHz, CDCl3, 25 °C) δ 153.7, 153.1, 152.2, 120.1, 120.0, 119.7, 117.8, 95.3, and 56.2. 4,4′-Bis(4-methoxyphenoxy)diphenyl ether (**L-4-OMe**) (86% yield), 4,4′-bis[4-{4-(methoxymethoxy)phenoxy}phenoxy]diphenyl ether (**L-6-OMOM**) (82% yield), 1,4-diphenoxybenzene (94% yield), and 4,4′-diphenoxydiphenyl ether (90% yield) were prepared similarly. **L-4-OMe**: ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 6.98−6.92 (m, 12H), 6.87 (d, 4H, J = 9.0 Hz), 3.80 (s, 6H); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$, 25 °C) δ 155.8, 153.9, 152.9, 150.9, 120.3, 119.8, 119.2, 114.9, and 55.7. **L-6-OMOM**: ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 7.03−6.91 (m, 24H), 5.14 (s, 4H), 3.50 (s, 6H); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$, 25 °C) δ 153.7, 153.3, 153.1, 152.8, 152.0, 120.1, 119.9, 119.9, 119.8, 119.5, 117.7, 95.1, and 56.1. 1,4-Diphenoxybenzene: ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 7.3−7.38 (m, 4H), 7.06−7.12 (m, 2H), and 6.98−7.02 (m, 8H); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$, 25 °C) δ 155.8, 153.9, 152.9, 150.9, 120.3, 119.8, 119.2, 114.9, and 55.7. 4,4′-Diphenoxydiphenyl ether: ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 7.36−7.30 (m, 4H), 7.11−7.06 (m, 2H), and 7.02−6.98 (m, 12H); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$, 25 °C) δ 157.8, 153.2, 152.5, 129.7, 123.0, 120.5, and 119.8.

4,4′-Bis(4-hydroxyphenoxy)diphenyl Ether. **A: From 4,4′-Bis-[4-(methoxymethoxy)phenoxy]diphenyl Ether.** To a 100-mL round-bottomed flask were added 2-propanol (10 mL), dichloromethane (10 mL), 4,4′-bis[4-(methoxymethoxy)phenoxy]diphenyl ether (0.21 g, 0.44 mmol), and concd HCl (1 drop), and the mixture was refluxed for 3 h. Volatiles were evaporated, and the residue was washed with water to obtain 4,4′-bis(4-hydroxyphenoxy)-diphenyl ether as a white solid (0.17 g, 0.44 mmol, 98% yield). 4,4′-Bis[4-(4-hydroxyphenoxy)phenoxy]diphenyl ether was prepared similarly (99% yield): ^{1}H NMR (300 MHz, DMSO-d_6, 25 °C) δ 9.34 (s, 2H), 7.01−6.96 (m, 12H), 6.90 (d, 4H, J = 9.0 Hz), 6.86 (d, 4H, J = 9.0 Hz), and 6.75 (d, 4H, J = 9.0 Hz); $^{13}C\{^1H\}$ NMR (75.5 MHz, DMSO-d_6, 25 °C) δ 154.9, 154.6, 153.8, 153.4 152.7 149.4, 121.4 120.9, 120.8, 120.6 119.6, and 117.2.

B: From 4,4′-Bis(4-methoxyphenoxy)diphenyl Ether. To a 100-mL round-bottomed flask containing 4,4′-bis(4-methoxyphenoxy)diphenyl ether (1.1 g, 2.65 mmol) and chloroform (60 mL) was added BBr_3 (dichloromethane solution (1.0 M), 15.5 mL) dropwise over a period of 1 h at 0 °C. The mixture was gradually warmed to room temperature and stirred for 2 h. The volatiles were evaporated, and the residue was washed with water to afford 4,4′-bis(4-hydroxyphenoxy)diphenyl ether as a white solid (0.95 g, 2.46 mmol, 97% yield): ^{1}H NMR (300 MHz, DMSO-d_6, 25 °C) δ 9.39 (s, 2H), 6.93 (d, 4H, J = 9.0 Hz), 6.87 (d, 4H, J = 9.0 Hz), 6.83 (d, 4H, J = 9.0 Hz), and 6.73 (d, 4H, J = 9.0 Hz); $^{13}C\{^1H\}$ NMR (75.5 MHz, DMSO-d_6, 25 °C) δ 154.8, 154.6, 153.0, 149.5, 121.3, 120.6, 119.6, and 117.1.

Cyclic Hexa(*p*-phenylene oxide). To a 100-mL round-bottomed flask were added 4,4′-(4-hydoxyphenoxy)diphenyl ether (101 mg, 0.25 mmol), 4,4′-diiododiphenyl ether (96 mg, 0.25 mmol), CuI (6 mg, 0.03 mmol), *N*,*N*-dimethylglycine hydrochloride (14 mg, 0.1 mmol), Cs_2CO_3 (0.33 g, 1.0 mmol), and DMF (10 mL), and the mixture was stirred at 100 °C for 22 h. Volatiles were evaporated, and the residue was extracted with chloroform, which was washed three times with water and dried over $MgSO_4$, and volatiles were evaporated to obtain cyclic hexa(*p*-phenylene oxide) as a white solid (30 mg, 0.044 mmol, 17% yield). The single crystals of cyclic hexa(*p*-phenylene oxide) were obtained by recrystallization from dichloromethane/hexane. The macrocycles provided HRMS data that are consistent with the molecular formula. Elemental analyses of **C-7**−**C-10**, however, led to the results showing that they contain the solvent in a nonstoichiometric ratio and that the formula based on the analytical results may disagree with the crystallographic results. It indicates that the crystals undergo elimination of the solvent in part during drying them under vacuum and that the analytical results are for the metastable solid containing partially eliminated solvent. Formulas of **C-7**−**C-10** containing $CHCl_3$ are calculated from C/H ratios only. **C-6**: ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 6.85; $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$, 25 °C) δ 154.0 and 120.0. Anal. Calcd for $C_{36}H_{24}O_6$: C, 78.25; H, 4.38. Found: C, 78.07; H, 4.51.

Other cyclic oligo(*p*-phenylene oxide)s were prepared similarly. **C-7**: ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 6.94; $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$, 25 °C) δ 153.3, and 120.0; HR MS (FAB+) *m*/*z* calcd for $C_{42}H_{28}O_7$ 644.1835, found 644.1832. Anal. Calcd for $C_{42}H_{28}O_7{\cdot}(CHCl_3)_{0.11}$: C, 76.77; H, 4.30; Cl, 1.94. Found: C, 76.46; H, 4.05, Cl, 1.02. **C-8**: ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 6.93; $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$, 25 °C) δ 153.0 and 120.0; HR MS (FAB+) *m*/*z* calcd for $C_{48}H_{32}O_8$ 736.2097, found 736.2106. Anal. Calcd for $C_{48}H_{32}O_8{\cdot}(CHCl_3)_{1.7}$: C, 63.52; H, 3.61. Found: C, 63.82; H, 3.61. **C-9**: ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 6.953; $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$, 25 °C) δ 153.3 and 120.0; HR MS (FAB+) *m*/*z* calcd for $C_{54}H_{36}O_9$ 828.2359, found 828.2348. Anal. Calcd for $C_{54}H_{36}O_9{\cdot}(CHCl_3)_{0.83}$: C, 70.97; H, 4.00; Cl, 9.51. Found: C, 70.58; H, 3.72, Cl, 8.57. **C-10**: ^{1}H NMR (300 MHz, CDCl3, 25 °C): δ 6.95. $^{13}C\{^1H\}$ NMR (75.5 MHz, CDCl3, 25 °C): δ 153.1 and 119.8. HR MS (FAB+) *m*/*z* calcd for $C_{60}H_{40}O_{10}$ 920.2622, found 920.2587. Anal. Calcd for $C_{60}H_{40}O_{10}{\cdot}(CHCl_3)_{0.3}$: C, 75.70; H, 4.25. Found: C, 75.41; H, 4.66.

Supporting Information Available: Crystal structure determination, thermogravimetric analysis, and differential scanning calorimetry of macrocycles and crystallographic data for **C-6**, **C-7**, **C-8**, and **C-9** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

JO0609982