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Dibenzotetraaza Crown Ethers: A New Family of Crown Ethers Based on *o*-Phenylenediamine[†]

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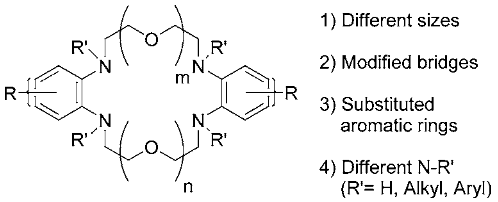
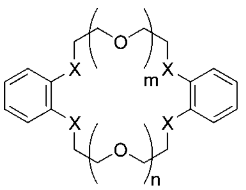


Dibenzotetraaza (DBTA) crown ethers possess two *o*-phenylenediamine moieties. They are homologues of dibenzo crown ether phase-transfer catalysts and were prepared from the condensation of benzimidazoles with oligo(ethyleneglycol) dichlorides and oligo(ethyleneglycol) ditosylates. Compounds with ring sizes ranging from 18-crown-6 to 42-crown-14 were prepared. In addition, various altered benzimidizoles were used to produce DBTA crown ethers with modified substituents and ether bridges, as well as benzimidazolidine crown ethers. The synthetic approach presented here proved to be a convenient route to a new family of crown ethers with overall yields of up to 48% based on the benzimidazole. Yields for the ring-closing step were generally high, ranging from 51% to 94%, without the need for high-dilution conditions. Reaction of the DBTA crown ethers with alkyl and benzyl halides was found to be a facile way to obtain the corresponding tetra(*N*-organyl) compounds. Picrate extraction studies were carried out to determine phase-transfer catalytic capabilities. Extraction efficiencies for alkali-metal ions were lower than those for dibenzo-18-crown-6. Efficiencies were higher for other metal ions, with some selectivity for Pb^{2+}. Tetra(*N*-methyl) DBTA-18-crown-6 generally exhibited higher extraction efficiencies than its N−H analogue, but the selectivity was lower.

Introduction

Since their discovery by Pedersen over 35 year ago,[1] crown ethers, large ring molecules with structures derived from cyclic ethyleneglycol $(OCH_2CH_2)_n$, have established a place in synthetic and analytical chemistry.[2] Crown compounds are routinely employed as phase-transfer catalysts (PTC) for organic synthesis. Analytical chemistry makes use of crown ethers in ion-selective sensors.[3] During a recent study to investigate corrosion of steels coated by crown ethers, we became interested in comparing commercially available dibenzo crown ethers (**1**) and aza crown ethers with mixed aza−oxo crown ethers, namely dibenzotetraaza (DBTA) crown ethers (**2**).[4]



1 X= O
2 X= NH, NR

The ability of a crown ether macrocycle to complex a (metal) cation depends chiefly on the size of the macrocycle and the number and type of the heteroatoms. Optimal complexation is achieved when the macrocycle can easily “wrap around” the cation, thus increasing the electronic interaction between the heteroatoms and the cation. Generally, oxygen-containing crown ethers exhibit superior complexation of alkaline−metal cations, whereas nitrogen- and sulfur-containing macrocycles favor transition−metal cations.[2a−d,5]

Despite the very large number of crown ethers based on catechol (i.e., benzo and dibenzo crown ethers) and nitrogen crown analogues,[2a−d,6] only a few mixed aza−

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oxo crown ethers based on *o*-phenylenediamine are reported in the literature:[7−9] Yields of these mixed aza−oxa benzodiaza (BDA) crown ethers are generally low to moderate.[10] Only two DBTA-18-crown-6 and one tetra(*N*-methyl) DBTA-18-crown-6 syntheses are reported in the literature.[11−13] This further underscores the need for the development of a general, reliable, high-yield synthesis for *o*-phenylenediamine analogues.

Results and Discussion

Synthetic Considerations. The synthesis of dibenzo oxo crown ethers such as dibenzo-18-crown-6 is based on catechol. Syntheses of dibenzotetraaza crown ethers based on *o*-phenylenediamine seem impractical because various side reactions of the amine groups can be expected. This is confirmed by the reports on BDA crown ether syntheses.[8c] Preparation of crown compounds using *N*,*N′*-diorganyl-*o*-phenylenedamine with an ether-bridge-forming molecule, such as oligo(ethyleneglycol) dichloride, can still lead to mixtures of crown ethers of different sizes. After the first nitrogen reacts with the chlorinated glycol, the second nitrogen and the second chloride leaving group are in close proximity. This can favor the formation of (1:1) benzodiaza crown ether over the desired (2:2) dibenzotetraaza crown ether. To have better control over ring formation, ether bridges should be introduced stepwise. This synthetic course requires the use of a highly protected *o*-phenylenedamine. Benzimidazole is essentially an *o*-phenylenediamine protected through condensation with formic acid.[14] The two nitrogen atoms in benzimidazole possess very different reactivities.[11,15−17] Under basic conditions, only one nitrogen reacts with the ether-bridge-forming oligo(ethyleneglycol) dichloride. In a second step, under different conditions, namely refluxing nitromethane, the ring is closed by introduction of the second bridge with oligo(ethyleneglycol) ditosylate. Shi and co-workers studied the chemistry of radicals obtained from such benzimidazolium salts after electrochemical reduction.[15] Díez-Barra and colleagues used similar synthetic strategies in their studies of benzimidazol-2-ones.[16] Ecke et al. used the approach for the preparation of DBTA-18-crown-6.[11] We decided to focus our efforts on further exploring and expanding this methodology to include DBTA crown ethers (**2**) with different sizes, modified ether bridges, and various substituents.

Synthesis

The general reaction sequence leading to the DBTA crown ethers (**2**) is shown in Scheme 1.[11] Benzimidazoles (**4**) were either commercially available or prepared from the corresponding diamines (**3**). These benzimidazoles were treated with the readily available dichloroethers (**5**) to form the bis(benzimidazolyl)ethers (**6**) under PTC conditions using either potassium hydroxide (method **A**)[11] or potassium carbonate (method **B**) as the base. Reaction of **6** with ditosylates (**7**) formed the macrocyclic bis(benzimidazolium) salts (**8**). The stepwise introduction of the ether bridges between the benzimidazole moieties allowed the synthesis of *symmetric* ($m = n$) and *unsymmetric* crown ethers ($m \neq n$). The DBTA crown ethers (**2**) were obtained by treating **8** with concentrated alcoholic hydroxide solutions at elevated temperatures (Table 1). Crown ethers with one substituent at each aromatic ring were obtained as a mixture of two isomers: The substituents could be syn or anti. Alternatively, the salts (**8**) could be reduced with sodium borohydride to yield the benzimidazolidine crown ethers (**9**) (Table 2). Treatment of the DBTA crown ethers (**2**) with alkyl or aryl halides in the presence of powdered potassium carbonate yielded the tetra(*N*-organyl) DBTA crown ethers (**10**) (Table 3).

The preparation of bis(benzimidazolyl)ethers (**6**) using method **A** was preferred for the preparation of smaller, unsubstituted DBTA crowns. The reactions were com-

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(2) See, for example: (a) *Crown Compounds: Toward Future Application*; Cooper, S. R., Ed.; VCH Publishers: New York, 1992. (b) *Crown ethers and analogous compounds*; Hiraoka, M., Ed.; Elsevier: Amsterdam, New York, 1992. (c) *Cation binding by macrocycles: complexation of cationic species by crown ethers*; Inoue, Y., Gokel, G. W., Eds.; M. Dekker: New York, 1990. (d) *Aza-crown macrocycles*; Bradshaw, J. S., Krakowiak, K. E., Izatt, R. M., Eds.; Wiley & Sons: New York, 1993. (e) *Crown ethers and analogues*; Weber, E., Toner, J. L., Goldberg, I., Fögtle, F., Laidler, D. A., Stoddard, J. F., Bartsch, R. A., Liotta, C. L., Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989. (f) Fabre, B.; Simonet, J. *Coord. Chem. Rev.* **1998**, *178−180*, 1211. (g) Bencini, A.; Bianchi, A.; Garcia-España, E.; Micheloni, M.; Ramirez, J. A. *Coord. Chem. Rev.* **1999**, *188*, 97. (h) Krakowiak, K. E.; Bradshaw, J. S.; Zameckakrakowiak, D. J. *Chem. Rev.* **1989**, *89* (4), 929. (i) Krakowiak, K. E.; Bradshaw, J. S.; Izatt, R. M. *Synlett* **1993**, 611.

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SCHEME 1. General Preparation of DBTA Crown Ethers 2 and Benzimidazolidine Crown Ethers 9

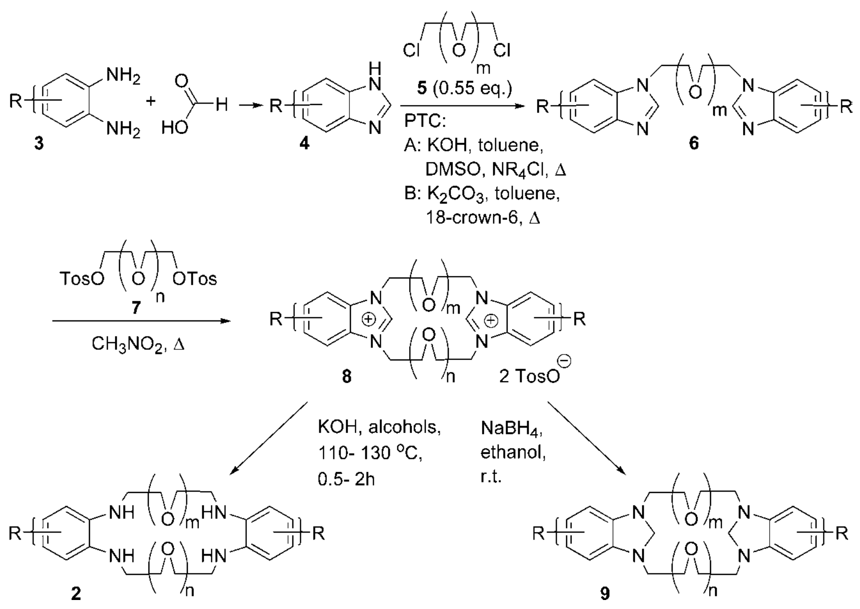
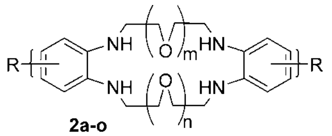
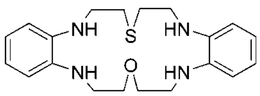


TABLE 1. DBTA Crown Ethers 2 Prepared


2a-o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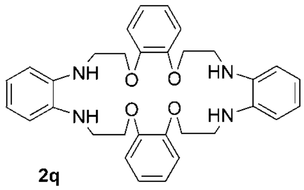
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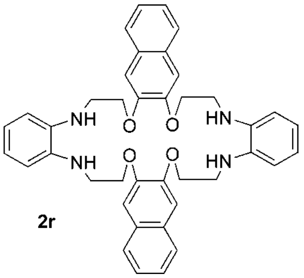

2r

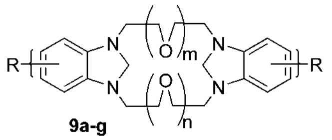
						ring-closing step[c]	
compd[a]	R	size		overall yield[b] (%)	mp (°C)	concn (mol/L)	yield (%)
2a	H, H	$m = n = 1$	18-crown-6	38	185−188	0.217	67
2b	H, H	$m = n = 2$	24-crown-8	26	124−125	0.063	51
2c	H, H	$m = n = 3$	30-crown-10	27	110−111	0.029	86
2d	H, H	$m = n = 4$	36-crown-12	43	oil	0.014	75
2e	H, H	$m = n = 5$	42-crown-14	42	oil	0.007[d]	74
2f	H, H	$m = 1; n = 2$	21-crown-7	32	122−123	0.049	77
2g	H, H	$m = 2; n = 3$	27-crown-9	16	oil	0.017	65
2h	Me, Me	$m = n = 1$	18-crown-6	48	225−226	0.065	83
2i	Me, Me	$m = 1; n = 2$	21-crown-7	27	154	0.065	87
2j	Me, H	$m = n = 1$	18-crown-6	20	188−189	0.125	54
2k	MeO, H	$m = n = 1$	18-crown-6	25	160	0.055[d]	94
2l	Cl, H	$m = n = 1$	18-crown-6	30	205−209[e]	0.045[d]	87
2m	F_3C, H	$m = n = 1$	18-crown-6	8	55−65	0.040[d]	54
2n	O_2N, H	$m = n = 1$	18-crown-6	*f*	*f*	0.050	87
2o[g]	H_2N, H	$m = n = 1$	18-crown-6	8[h]	*f*	*g*	*g*
2p			18-crown-6	27	168−169	0.017	75
2q			24-crown-8	44	208[e]	0.027	60
2r			24-crown-8	37	228−230[e]	0.027	68

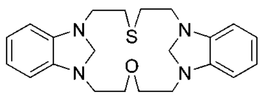
[a] Crown ethers with mixed substituents (**2j**−**o**) were obtained as a mixture of two isomers. [b] Isolated yield based on benzimidazole **4**, not optimized. [c] Formation of the ditosylate salt **8**. [d] Reagents were mixed in cold CH_3NO_2 and slowly added to hot reaction vessel. [e] Decomposition. [f] Not determined. [g] Prepared from **2n**. [h] Based on benzimidazole **4a**.

plete after 12 h. Most other preparations used the milder method **B** where reaction times ranged up to several days.

For the preparation of **8** from **6**, oligo(ethyleneglycol) ditosylates (**7**) were preferred over dichloroethers (**5**) because they usually delivered crystalline salts. Diver-

TABLE 2. Benzimidazolidine Crown Ethers 9 Prepared


9a-g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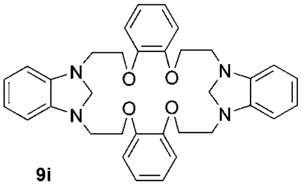
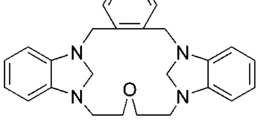
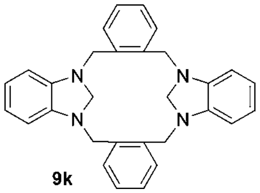

9i

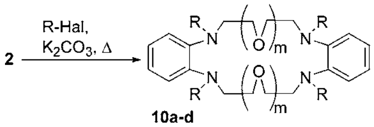

9j


9k

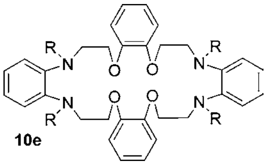
compd[a]	R	size		yield[b] (%)	mp (°C)
9a	H, H	$m = n = 1$	16-crown-6	77	137−140
9b	H, H	$m = n = 2$	22-crown-8	82	123−127
9c	H, H	$m = n = 3$	28-crown-10	40	86−94
9d	Me, Me	$m = n = 1$	16-crown-6	82	182−184[c]
9e	Me, Me	$m = 1$; $n = 2$	19-crown-7	46	98−110[c]
9f	F_3C, H	$m = n = 1$	16-crown-6	91	>100[c]
9g	O_2N, H	$m = n = 1$	16-crown-6	91	>155[c]
9h			16-crown-6	81	120−130[c]
9i			22-crown-8	46	230−234[c]
9j			15-crown-5	90	127−135[c]
9k			14-crown-4	82	170−172[c]

[a] Crown ethers with mixed substituents (**9f**,**g**) were obtained as a mixture of two isomers. [b] Isolated yield for reduction, not optimized. [c] Decomposition.

TABLE 3. Tetra(*N*-organyl) DBTA Crown Ethers 10 Prepared



10a-d


10e

compd	size	R	yield[a] (%)	mp (°C)	reaction steps[b] (time, temp)	
10a	$m = 1$	Me	72	72−73	(1) 5 h, rt	(2) 1 day, 35 °C
10b	$m = 1$	Et	82	102−103	(1) 12 h, 50−55 °C	(2) 1 day, 65−68 °C
10c	$m = 1$	Bz	65	resin	(1) 2 days, 60−75 °C	(2) 12 h, 95 °C
10d	$m = 2$	Et	21	32−33	(1) 20 h, 65−67 °C	
10e		Me	31	oil	(1) 12 h, rt	(2) 12 h, 30−35 °C

[a] Not optimized. [b] Monitored by TLC (thin-layer chromatography); reaction times varied depending on stirring, coarseness of K_2CO_3, and exact temperature.

gently, large crown salts **8d**,**e** with ring sizes of 34 and 40 atoms, respectively, and **8i** with unsymmetric ether bridges were obtained as viscous oils. Purification was achieved via recrystallization or extraction of unreacted starting materials with an organic solvent.

It is worth mentioning that high-dilution conditions were not necessary for the ring-closing step:[18] Concentrations of less than 0.001 mol/L are usually considered "high dilution". We successfully employed concentrations of up to 0.2 mol/L without detection of any contamination by polymers or larger ring systems in the isolated salts. This may be attributed to the formation of a benzimidazolium cation, acting as an internal template for the ring closing. Lower concentrations were chosen for the larger crown ethers to minimize possible side reactions (i.e., oligo- and polymerization) in the case of these sterically more flexible molecules. The yields for the ring-closing step in the case of the 17 crown ethers listed in Table 1 ranged from 51% to 94%.

Crown Ethers 2. A. Unsubsituted Crown Ethers (2a−g). These compounds were prepared by treating the salts (**8**) with excess potassium hydroxide in propanol or an ethanol−propanol mixture at 110 °C for 1−2 h. The smaller crown ethers **2a**−**c**,**f** were obtained as crystalline solids, and the larger crown ethers **2d**,**e**,**g** were obtained as viscous oils. Purification consisted of simple crystallization or washing with water. All crown ethers were stable under ambient conditions.

B. Crown Ethers with Substituted Aromatic Rings (2h−o). The preparation of crown ethers with electron-donating substituents proceeded smoothly, and they were obtained as solids that were stable under ambient

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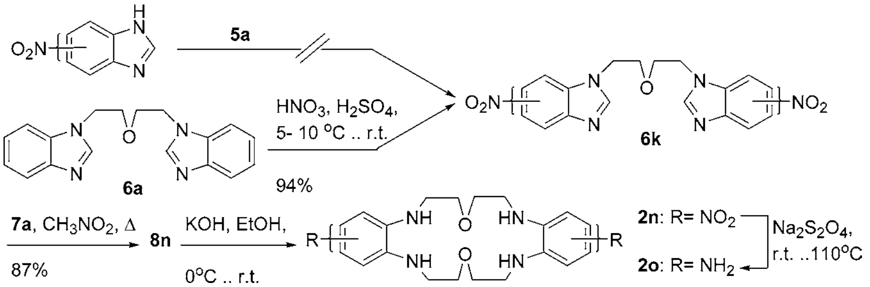
[18] Ecke and co-workers carried out the ring-closing step in 0.7 M solution.[11] The lower yield of 50% (vs 67% reported here) might be due to side reactions at the very high concentration.

SCHEME 2. Modified Preparation of DBTA Crown Ethers 2n and 2o



conditions. They were stable in solution for weeks, as well, unless exposed to air.

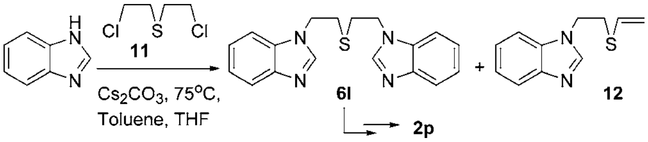
Tetramethyl DBTA crown ethers **2h**,**i** were obtained as hydrophobic solids. Compound **2h** was prepared in a high overall yield of 48% (based on the benzimidazole). This was the highest yield obtained for any crown ether prepared. Compound **2i** is an example of an unsymmetric crown ether containing substituted aromatic rings. It was necessary to carry out the transformation of salts **8h**,**i** to **2h**,**i** at 130 °C to drive the reaction to completion. These conditions were then used successfully for most of the other substituted crown ethers.

The synthesis and isolation of crown ethers with electron-withdrawing substituents proved to be more challenging. They were prone to oxidation in solution when exposed to air, with the exception of dichloro DBTA crown ether **2l**. Crown ethers **2m**−**o** were characterized by means of NMR spectroscopy.

The preparation of dinitro DBTA crown ether **2n** required considerable modification of the general reaction scheme (Scheme 2). Nitrobenzimidazole did not react with the dichloroether **5a** to form bis(benzimidazolyl)-ether (**6k**). However, it was reported in the literature that *N*-methylbenzimidazole is readily nitrated at the 5- or 6-position by using a mixture of concentrated nitric acid and sulfuric acid at room temperature.[19] Furthermore, it has been shown that compounds with ether bridges similar to those of **6a** are stable in concentrated sulfuric acid at 100 °C for 3 days.[20] On the basis of this information, the bis(benzimidazolyl)ether (**6a**) was successfully nitrated in high yield under mild conditions. The transformation to the macrocyclic salt (**8n**) was readily accomplished. Unfortunately, decomposition was observed when **8n** was treated with alcoholic potassium hydroxide at elevated temperatures. It was found that **8n** readily reacts at 0 °C. Attempts to isolate and purify **2n** were unsuccessful, although the ^{1}H NMR spectrum of the crude reaction mixture was in good agreement with the structure of **2n**.

To confirm the formation of dinitro DBTA crown ether (**2n**), reduction to the diamino DBTA crown ether (**2o**) was performed. Sodium dithionite was added to the neutralized crude mixture, and the temperature was increased to 110 °C. Thin-layer chromatography (TLC) showed only *one* spot, and extraction yielded a small amount of a lightly tan-colored solid. ^{1}H and ^{13}C NMR spectra were consistent with the structure expected for **2o**. The compound was stable as a solid but decomposed slowly in $CDCl_3$ during the acquisition of the NMR spectra.

SCHEME 3. Reaction of Benzimidazole Bis(chloroethyl)thioether (11) Yielding the Desired Thioether 6l, Along with the Ethyl Vinyl Sulfide 12



C. Crown Ethers with Modified Ether Bridges (2p−r). The preparation of DBTA oxathia-18-crown-6 (**2p**) followed the general synthesis (Scheme 1) with some modifications of the first step (Scheme 3): Formation of the bis(benzimidazolyl)thioether (**6l**) required close control of the reaction temperature to maximize the yield. It was found that **6l** can be obtained in a yield of 47% when Cs_2CO_3 is used as the base at 75 °C in a toluene/THF mixture. At lower temperatures, the reaction proceeded very slowly, and at higher temperatures, the yield dropped considerably. The elimination product 2-(1′-benzimidazolyl)ethyl vinyl sulfide (**12**) was isolated, thus confirming the tendency of 2,2′-bis(chloroethyl)thioether (**11**) to undergo elimination at higher temperatures (Scheme 3). Compound **6l** was a stable solid, melting at 172−174 °C. Further synthesis of **2p** proceeded smoothly; it was obtained as a stable, microcrystalline solid.[21]

Tetraaryl tetraaza crown ethers **2q**,**r** were prepared following the synthesis outlined in Scheme 1. Their bis(benzimidazolyl)ether precursors (**6m**,**n**) were synthesized according to method **B**. The macrocyclic salts (**8p**,**q**) had moderate solubility in water and methanol and were nearly insoluble in ethanol or other longer-chain alcohols. The latter solvents were required to reach the necessary temperatures for the complete transformation to the crown ethers. To circumvent this problem, the salts were first treated with potassium hydroxide in refluxing methanol. Next, *n*-butanol and more potassium hydroxide were added, thus allowing for reflux at a higher temperature. Compounds **2q**,**r** were much less soluble than the other crown ethers prepared. The naphtha compound **2r** was soluble only in trace amounts in common organic solvents (including hot DMSO).

Benzimidazolidine Crown Ethers (9). Benzimidazolidine crown ethers (**9**) were obtained by reduction of

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(19) Viktor, M.; Dušan, I. *Bull. Soc. Chim. Belg.* **1996**, *105* (4), 213.

(20) Biernat, A. F.; Luboch, E. *Tetrahedron* **1984**, *40* (10), 1927.

(21) Attempts to synthesize a tetraazadithio crown ether were unsuccessful. The formation of the dithio-benzimidazolium salt was studied on reactions of **11** with bis(benzimidazolyl)ether **6a**. The relatively harsh conditions required in this step (refluxing CH_3NO_2) made the salt formation impossible. Instead, decomposition was observed. No attempt was made to use the ditosylate instead of **11**, because it had been described as being considerably *less* stable than **11** and decomposing at room temperature. See: Aizenberger, M.; Turculet, L.; Davis, W. M.; Schattenmann, F.; Schrock, R. R. *Organometallics* **1998**, *17* (22), 4795.

the macrocyclic salts (**8**):[11,22] they precipitated almost instantaneously when $NaBH_4$ was added to an ethanolic solution of **8** and were isolated as stable solids (Table 2). The preparation of the dinitro benzimidazolidine crown ether (**9g**), a brick red solid, provided further proof of the successful macrocyclic ring formation in the case of strongly electron-withdrawing substitutents.

Tetra(*N*-organyl) DBTA Crown Ethers (10). One synthesis of tetra(*N*-methyl) DBTA-18-crown-6 (**10a**) has been previously reported.[13] It uses *N,N'*-dimethyl-*o*-phenylenediamine as the starting material and employs dihydrofuran to form the ether bridges in two successive ozonolysis/reductive alkylation steps. The authors report a yield of 40% for the two steps. This approach is limited because few *N,N'*-diorganyl-*o*-phenylenediamine derivatives are available. In addition, the use of dihydrofuran for the formation of the ether bridges limits this approach to the formation of a tetra(*N*-methyl) DBTA-18-crown-6. To circumvent such limitations, we successfully determined general synthesis conditions for tetra(*N*-organyl) DBTA crown ethers (**10**).

Initially, we attempted to obtain crown ethers, **10,** from their N−H analogues, **2**, via reductive alkylation using an aldehyde and sodium cyanoborohydride in the presence of a small amount of acid in acetonitrile at room temperature.[23,24] However, it was difficult to remove the byproducts. The impurities were most likely small amounts of incompletely alkylated crown ethers (as indicated by TLC). It was difficult to reliably achieve full conversion to the tetra(*N*-alkyl) product, even when a very large excess of aldehyde (up to 60 equiv) and sodium cyanoborohydride was used. The impurities could be removed by careful column chromatography on basic aluminum oxide. Unfortunately, this method of purification significantly decreased the yield.

Low conversion and cumbersome workup led us to study the direct alkylation (or arylation) where the N−H crown ethers (**2**) were simply mixed with an excess of alkyl (or aryl) halide. Sluggish reactions were encountered when solely **2** and the halide were mixed and gently heated. However, the reaction proceeded faster when an excess of finely powdered K_2CO_3 was added to the reaction mixture. Under these conditions, the formation of the tetra(*N*-organyl) crown ethers (**10**) proceeded quickly, with slow further conversion to the undesirable quaternary ammonium salts, as indicated by TLC. Because the removal of partially substituted crown ethers was difficult, reactions were usually allowed to continue just until TLC indicated complete conversion. This usually led to the formation of a small amount of quaternary ammonium salts that could be removed easily by chromatography over a short aluminum oxide (basic) column. If the reaction was continued much beyond the point of completion indicated by TLC, the yields began to drop. All tetra(*N*-organyl) DBTA crown ethers (**10**) prepared were stable under ambient conditions (Table 3).

It is hypothesized that the addition of K_2CO_3 affects the outcome of the reaction by neutralizing hydrogen ions, thereby preventing protonation of the amines, and by supplying potassium cations which may reduce the nucleophilicity of tertiary nitrogens by forming a host−guest complex with the crown ether. The latter effect has been described for nickel complexes of aza crowns.[25]

Yields generally benefited from a stepwise increase of the reaction temperature, as compared with running the reactions at a higher temperature from the beginning: At the lower temperature, mono(*N*-organyl) and di(*N*-organyl) crown ethers are readily formed. At higher temperatures, the increased steric hindrance is overcome and the tri(*N*-organyl) and, eventually, the tetra(*N*-organyl) compounds are formed. If the reactions are run at a high temperature from the start, steric hindrance plays a lesser role and the formation of quaternary ammonium salts (especially of the mono(*N*-organyl) and di(*N*-organyl) crown ethers) is more likely. This explanation is consistent with the low yield of **10d**.

Hydrolysis of Benzimidazolium Salts: Mechanism

In early attempts to obtain the tetramethyl DBTA crown ether **2h** from the benzimidazolium salt **8h**, the reaction was carried out at 110 °C affording diformamide (**13**). It was characterized by ^1H NMR spectroscopy, HR−MS, and elemental analysis. The ^1H NMR spectrum shows a characteristic singlet at $\delta = 8.09$ ppm corresponding to the formamide proton. At 130 °C the desired **2h** was readily obtained (Scheme 4).

A similar observation was made for the formation of tetrabenzotetraaza-24-crown-8 (**2q**). Due to limited solubility of the macrocyclic salt (**8p**) in higher-boiling alcohols, the salt had to be treated with potassium hydroxide in refluxing methanol. When the reaction was stopped at this point, the diformamide (**14**) was isolated (Figure 1). If, instead, *n*-butanol and additional potassium hydroxide were added and the reaction was continued under reflux at a higher temperature, the tetrabenzotetraaza-24-crown-8 (**2q**) was isolated.

The formation of a diformamide has also been reported by Ecke and co-workers for the synthesis of DBTA-18-crown-6 (**2a**) when carrying out the reaction in refluxing aqueous potassium hydroxide solution.[11] In refluxing potassium hydroxide ethanol/propanol solution, **2a** was obtained. It can be presumed that the change in solvents resulted in a change of the reaction temperature, as well.

Indications of a two-step process were also found for the synthesis of dinitro DBTA-18-crown-6 (**2n**) from the corresponding benzimidazolium salt (**8n**). Immediately after the addition of potassium hydroxide to an ethanolic solution of **8n** at −5 to 0 °C, TLC (Al_2O_3; CH_2Cl_2/ethanol, 95:5) showed one yellow spot ($R_f = 0.63$). This spot was attributed to the diformamide **15**. After an additional 3 h at 0 °C and 1 h at room temperature, a single orange spot ($R_f = 0.85$) was seen. This spot corresponded to the dinitro DBTA-18-crown-6 **2n**.

The formation of the diformamide points to the following two-step process: In the first, fast, step the hydroxide

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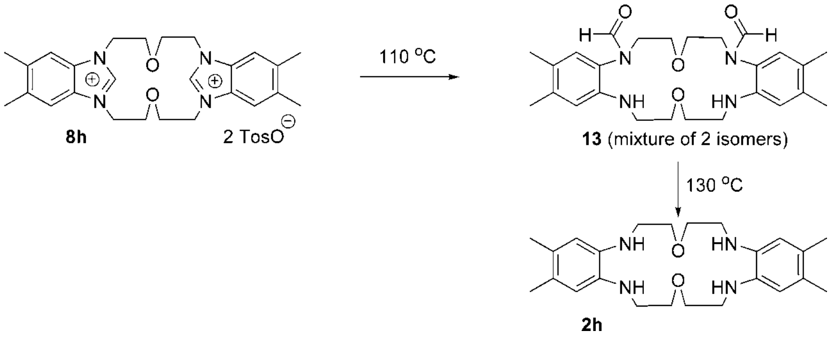
[22] The same reaction has been reported for *N,N'*-dialkylperimidinium salts. (Perimidine is obtained by treating 1,8-diaminohaphthalene with formic acid.) Pozharskii, A. F.; Kurasov, L. A.; Kuz'menko, V. V.; Popova, L. L. *J. Org. Chem. USSR, Engl. Transl.* **1981**, 884.

[23] Klaehn, D.-D.; Paulus, H.; Grewe, R.; Elias, H. *Inorg. Chem.* **1984**, *23* (4), 483.

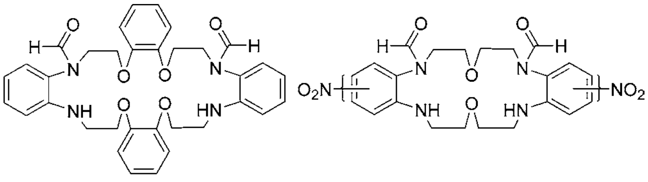
[24] Borch, R. F. *Organic Syntheses;* John Wiley & Sons: New York, 1988; Collect. Vol. VI*,* 499.

[25] *Metals and Ligand Reactivity*; Constable, E. C., Ed.; VCH Verlagsgesellschaft: Weinheim, Germany, 1996; pp 104−106.

SCHEME 4. Hydrolysis of the Benzimidazolium Salt 8 h at 110 °C Yielding the Formamide 13[a]



[a] Only at higher temperatures was it completely transformed into the DBTA crown ether **2h**.



14 (mixture of 2 isomers) **15** (mixture of isomers)

FIGURE 1. Hydrolysis of the corresponding precursor-benzimidazolium salts yielded **14** in refluxing methanolic potassium hydroxide solution and **15** in ethanolic potassium hydroxide solution at 0 °C, respectively.

ion attacks the −NCHN− bridge of the benzimidazolium cation to form the formamide. The second, slower, step consists of the attack of a second hydroxide molecule, yielding the desired crown ether and formic acid.

The observation that the formation of crown ethers with electron-donating substituents required higher temperatures than the formation of unsubstitued crown ethers is consistent with this mechanism. Further support of this explanation comes from the observation that electron-withdrawing substituents facilitated the reaction. Electron-donating substituents strengthen the formamide carbon−nitrogen bond, and electron-withdrawing substituents weaken it.

X-ray Structures

X-ray crystal structures were obtained for the benzimidazolium salt **8o** and the benzimidazolidine-28-crown-10 **9c** (Figure 2 and Supporting Information Figure S8). These results confirm that both small and large ring systems are obtained as well-defined compounds without contamination by other possible macrocycles.

Metal Ion Extraction Studies

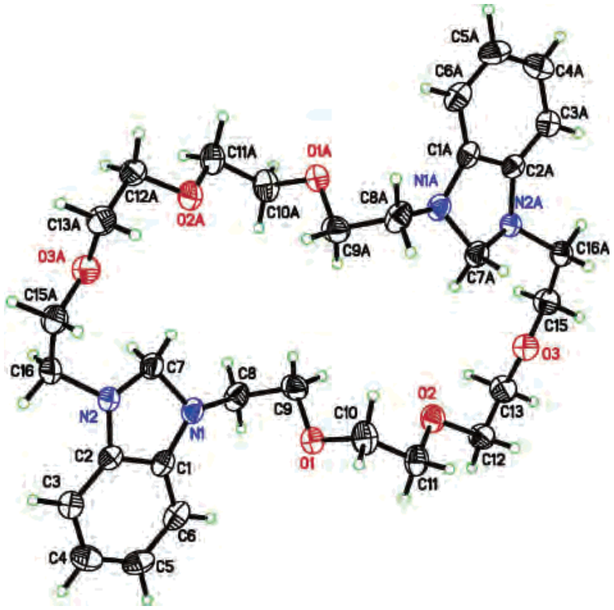


FIGURE 2. X-ray crystal structure of benzimidazolidine 28-crown-10 (**9c**). The data were collected at 150 K. At this temperature, the methylene bridges in the crystal were restricted to one position.

The utility of crown ethers as phase-transfer catalysts is based on their ability to form host−guest complexes with metal ions. Complexation ability and selectivity can be determined by extraction experiments. We decided to perform metal picrate extraction studies to screen some of the DBTA crown ethers synthesized.[26−28] This experiment exploits the fact that the crown ether is soluble in both the aqueous and the organic medium. When a crown ether molecule crosses over from the organic into the aqueous phase, it can complex a metal cation. Upon return to the organic layer, the host−guest (crown ether−cation) complex is accompanied by the picrate counterion. The efficiency of this extraction process can be measured by determining the amount of picrate extracted. When a pure organic solvent (CH_2Cl_2) and an aqueous solution of picric acid/metal salt are shaken, the aqueous layer is deeply yellow and the organic layer remains colorless. The yellow color is due to the picrate anion (λ_{max} = 356 nm). The addition of a crown ether to the organic layer causes the extraction of some of the metal picrate into the organic phase. The extent of this transfer can be determined by measuring the decrease of the picrate concentration in the aqueous phase using UV−vis spectroscopy.

Following Pedersen's studies, concentrations of 7.0×10^{-5} mol/L of crown ether in CH_2Cl_2 and 7.0×10^{-5} mol/L of picric acid in 0.1 M metal hydroxide were chosen for the alkali-metal ions.[26,27] Alkaline earth, transition, and

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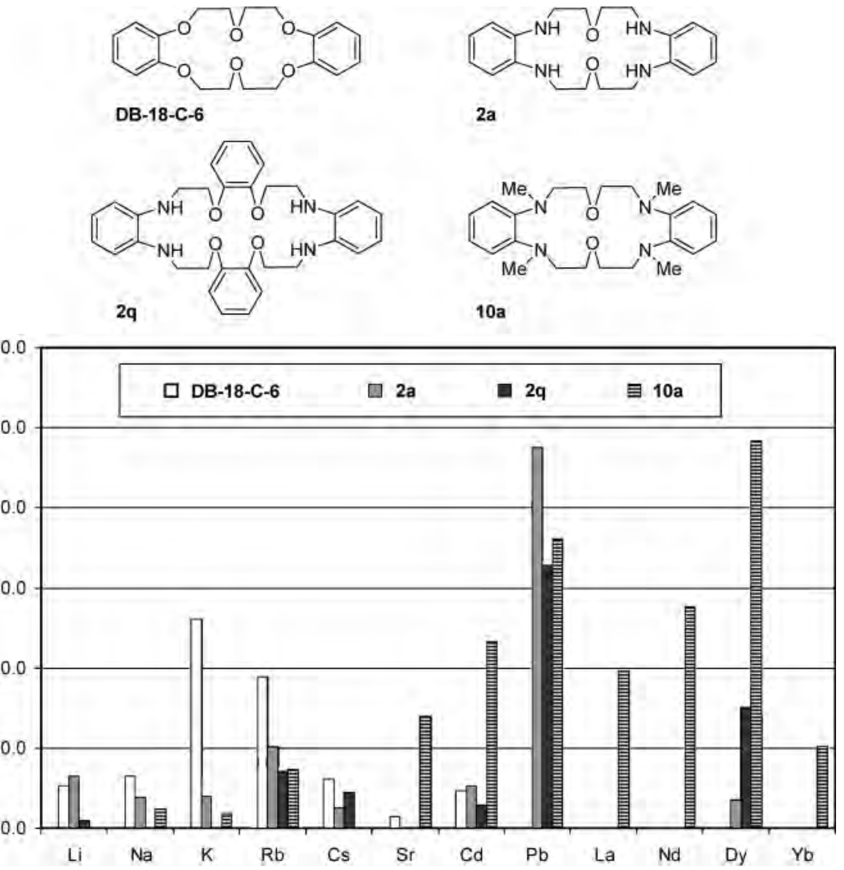
(26) Striley, C. A. Ph.D. Dissertation, University of Cincinnati, Cincinnati, OH, 1994.

(27) (a) Pedersen, C. J. *Chem. Scr.* **1988**, *28* (3), 229. (b) Pedersen, C. J. *Fed. Proc.* **1968**, *27* (6), 1305. (c) Okada, Y.; Kasai, Y.; Nishimura, J. *Synlett* **1995**, 85. And references therein.

(28) Inoue, Y.; Liu, Y.; Tong, L. H.; Tai, A.; Hakushi, T. *J. Chem. Soc., Chem. Commun.* **1989**, *20*, 1556.

CHART 1. Comparison of Metal Picrate Extraction Percentages of Dibenzo-18-crown-6 and Three Representative DBTA Crown Ethers



lanthanide metals were investigated as 0.03 M metal nitrate/7.0 × 10^{-5} M picric acid solutions. Under these conditions, absorption coefficients of <1 were obtained.

To exclude possible oxidation of the crown ethers in the organic solvent, the CH_2Cl_2 was flushed with inert gas and the crown ether solutions were prepared immediately prior to the extraction studies. Three representative crown ethers, **2a**, **2q**, and **10a**, were chosen for the studies (Chart 1). The extraction data were compared to a dibenzo-18-crown-6 (**DB-18-C-6**) solution as standard. The experiments were carried out in glass vials sealed with Teflon-lined caps. All data given are the averages of at least two independent experiments.

Extraction Results. DBTA crown ethers exhibited low alkali-metal ion extractability, as expected. The values were generally lower than those found for dibenzo-18-crown-6. Only Rb^+ was extracted to a small extent by all crown ethers.

The picrate-extraction values of some of the other (alkaline earth, transition, and lanthanide) metal ions tested were considerably higher for the DBTA crown ethers. The two N−H crown ethers (**2a**,**q**) showed remarkable extraction selectivity within the metal ion series tested. DBTA-18-crown-6 (**2a**) showed selectivity for Pb^{2+} over Cd^{2+}, Dy^{3+}, and the other (nonalkali) metal ions. Tetrabenzotetraaza-24-crown-8 (**2q**) showed a significant extraction preference for Pb^{2+} and Dy^{3+}. It was observed that the N−Me crown ether (**10a**) generally possessed higher extraction efficiency and lower selectivity than the N−H crown ether (**2a**). The tetra(*N*-methyl) DBTA-18-crown-6 (**10a**) extracted moderate to high amounts of all (nonalkali) metal picrates. In general, they were significantly higher than those observed for the N−H crown ethers **2a**,**q**, with the exception of Pb^{2+}: all three benzoaza crown ethers extracted high percentages of lead picrate. This higher selectivity for Pb^{2+} over Sr^{2+} is unexpected when one considers the comparable ionic radii (Pb^{2+} = 119 pm, Sr^{2+}= 118 pm).[29]

Conclusion

The presented synthetic approach proved to be a general, convenient preparation of crown ethers with *o*-phenylenediamine moieties. Dibenzotetraaza (DBTA) crown ethers (**2a**−**o**) were prepared from benzimidazoles in generally high overall yields without the need for high-dilution conditions. Ring closings were performed at concentrations of up to ~0.2 mol/L. Unsubstituted crown ethers, ranging from 18-crown-6 to 42-crown-14, were prepared. The smaller crown ethers were obtained as stable solids, whereas the larger ones were viscous oils. This synthetic pathway was extended to include crown ethers with modified ether bridges (i.e., bridges containing sulfur and bridges with catechol and 2,3-naphthalenediol moieties) (**2p**−**r**). Crown ethers with substituted aromatic rings (**2h**−**o**) were prepared by starting from the corresponding substituted *o*-phenylenediamines. Crown ethers with electron-donating and chlorine substituents were obtained as stable solids. The syntheses

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[29] Laminated *Periodensystem der Elemente;* Fluck, Heumann, Eds.; VCH Verlagsgesellschaft mbH: Weinheim, Germany, 1992.

of crown ethers with strongly electron-withdrawing substituents were more challenging. Spectroscopic evidence confirmed the formation of the desired products, but they were prone to oxidation, especially in solution. Several benzimidazolidine crown ethers (**9a**−**k**), DBTA crown ether analogues with methylene bridges between neighboring nitrogen atoms, were also synthesized.

Reductive alkylation of unsubstituted DBTA crown ethers was found to be only moderately successful. The removal of partially *N*-alkylated crown ethers was difficult and resulted in low yields. Direct alkylation with alkyl iodides or arylation with benzyl chloride in the presence of K_2CO_3 emerged as the method of choice. It proceeded smoothly and led to the formation of pure, stable tetra(*N*-organyl) crown ethers (**10a**−**e**).

Picrate extraction studies were performed to determine the complexation ability of some of the crown ethers prepared. As expected, the crown ethers extracted only very small amounts of alkali-metal ions. Within the group of metals tested, tetra(*N*-methyl) DBTA-18-crown-6 (**10a**) extracted moderate to high amounts of all alkaline earth-, transition-, and lanthanide-metal ions. The N−H crown ethers tested (**2a**,**q**) showed high extraction preference for Pb^{2+} and somewhat lower preference for Dy^{3+}.

Experimental Section

Preparation of Bis(benzimidazolium) Ditosylates 8: General Procedure. The procedure was adapted from ref 11. Equimolar amounts of the appropriate glycol **6** and ditosylate **7** were dissolved in nitromethane, and the mixture was heated at reflux for 0.5−7 days (concentrations: see Table 1). The reaction was monitored by TLC (Al_2O_3, CH_2Cl_2/ethanol 95:5). The salts were purified either by recrystallization from nitromethane or by dissolving them in water, followed by extraction of the unreacted starting materials with organic solvents.

1,1′:3,3′-Bis(di(ethyleneglycol))bis(benzimidazolium) Ditosylate (8a).[11] The salts were purified by recrystallization. Colorless crystals (67%); mp 282−283 °C (lit. 279.5−280.5 °C);[11] ^{1}H NMR (DMSO-*d*$_6$) δ 2.28 (s, 6H), 3.94 (br s, 8H), 4.70 (br s, 8H), 7.10 (d, 4H, *J* = 7.86 Hz), 7.49 (d, 4H, *J* = 8.12 Hz), 7.6 (m, 4H), 8.0 (m, 4H), 9.77 (s, 2H); ^{13}C NMR (DMSO-*d*$_6$) δ 20.9, 47.1, 67.0, 113.7, 125.6, 126.7, 128.2, 130.9, 137.8, 143.0, 145.8.

1,1′:3,3′-Bis(tri(ethyleneglycol))bis(benzimidazolium) Ditosylate (8b). The salts were purified by recrystallization. Colorless, fine crystals (51%); mp 241.0−241.5 °C; ^{1}H NMR (DMSO-*d*$_6$) δ 2.53 (s, 6H), 3.47 (br s, 8H), 3.77 (br s, 8H), 4.64 (br s, 8H), 7.07 (d, 4H, *J* = 7.61 Hz), 7.47 (d, 4H, *J* = 7.61 Hz), 7.68 (m, 4H), 8.05 (m, 4H), 9.51 (s, 2H); ^{13}C NMR (DMSO-*d*$_6$) δ 20.9, 46.6, 66.9, 69.2, 113.8, 125.6, 126.7, 128.2, 131.0, 137.7, 143.0, 145.8; MS (relative intensity) *m*/*z* 637 (M − TosO$^-$, 68.1%), 465 (M − 2TosO$^-$ − H$^+$), 107 (100%); HRMS calcd for $C_{33}H_{41}N_4O_7S$ 637.2696, found 637.3079. Anal. Calcd for $C_{40}H_{48}N_4O_{10}S_2$: C, 59.39; H, 5.98. Found: C, 59.54; H, 6.00.

1,1′:3,3′-Bis(tetra(ethyleneglycol))bis(benzimidazolium) Ditosylate (8c). The salts were purified by washing aqueous solution with CH_2Cl_2. Brittle, off-white solid (86%); mp 187−193 °C; ^{1}H NMR (DMSO-*d*$_6$) δ 2.25 (s, 6H), 3.29 (br s, 8H), 3.41 (br s, 8H), 3.81 (br s, 8H), 4.65 (br s, 8H), 7.08 (d, 4H, *J* = 7.64 Hz), 7.51 (d, 4H, *J* = 7.73 Hz), 7.60−7.70 (m, 4H), 8.00−8.10 (m, 4H), 9.59 (s, 2H); ^{13}C NMR (DMSO-*d*$_6$) δ 20.9, 46.8, 67.4, 69.6, 69.7, 113.9, 125.6, 126.6, 128.2, 131.1, 137.9, 142.9, 145.7; MS (relative intensity) *m*/*z* 725 (M − TosO$^-$, 70.7%), 553 (M − 2TosO$^-$ − H$^+$), 145 (100%); HRMS calcd for $C_{37}H_{49}N_4O_9S$ 725.3220, found 725.2766. Anal. Calcd for $C_{44}H_{56}N_4O_{12}S_2\cdot0.75\ CH_2Cl_2$: C, 55.94; H, 6.03. Found: C, 55.83; H, 6.17.

1,1′:3,3′-Bis(penta(ethyleneglycol))bis(benzimidazolium) Ditosylate (8d). The salts were purified by washing aqueous solution with CH_2Cl_2. Off-white, hard resin (75%); ^{1}H NMR (DMSO-*d*$_6$) δ 2.27 (s, 6H), 3.29 and 3.35−3.45 and 3.45−3.55 (br s, m, m, 24H), 3.75−3.85 (m, 8H), 4.60−4.70 (m, 8H), 7.09 (d, 4H, *J* = 7.64 Hz), 7.48 (d, 4H, *J* = 7.95 Hz), 7.60−7.80 (m, 4H), 8.00−8.15 (m, 4H), 9.57−9.65 (m, 2H); ^{13}C NMR (DMSO-*d*$_6$) δ 20.9, 46.8 (br), 67.5 (br), 69.7 (br), 114.0, 125.6, 126.7, 128.2, 131.2, 137.7, 143.0, 145.9; MS (relative intensity) *m*/*z* 813 (M − TosO$^-$, 10.8%), 321 (100%); HRMS calcd for $C_{41}H_{57}N_4O_{11}S$ 813.3745, found 813.3707. Anal. Calcd for $C_{48}H_{64}N_4O_{14}S_2\cdot1.5\ H_2O$: C, 56.96; H, 6.67. Found: C, 56.86; H, 6.63.

1,1′:3,3′-Bis(hexa(ethyleneglycol))bis(benzimidazolium) Ditosylate (8e). The salts were purified by washing aqueous solution with CH_2Cl_2. Yellowish, hard resinous solid (74%); ^{1}H NMR (DMSO-*d*$_6$) δ 2.27 (s, 6H), 3.36 (br s, 16H), 3.38−3.45 (m, 8H), 3.46−3.52 (m, 8H), 3.80−3.90 (m, 8H), 4.65−4.70 (m, 8H), 7.08 (d, 4H, *J* = 8.08 Hz), 7.49 (d, 4H, *J* = 7.66 Hz), 7.63−7.69 (m, 4H), 8.03−8.11 (m, 4H), 9.60−9.64 (m, 2H); ^{13}C NMR (DMSO-*d*$_6$) δ 20.9, 46.9 (br), 67.6 (br), 69.8 (br), 114.0, 125.6, 126.6, 128.2, 131.2, 137.7, 143.0, 145.9; MS (relative intensity) *m*/*z* 1095 (M + Na$^+$), 901 (M − TosO$^-$, 100%); HRMS calcd for $C_{45}H_{65}N_4O_{13}S$ 901.4269, found 901.4229. Anal. Calcd for $C_{52}H_{72}N_4O_{16}S_2$: C, 58.19; H, 6.76. Found: C, 58.07; H, 6.95.

1,1′-Di(ethyleneglycol)-3,3′-tri(ethyleneglycol)bis(benzimidazolium) Ditosylate (8f). The salts were purified by washing aqueous solution with CH_2Cl_2. Off-white, crystalline solid (77%); mp 78−84 °C; ^{1}H NMR (DMSO-*d*$_6$) δ 2.24 (s, 6H), 3.53 (s, 4H), 3.76 (t, 4H, *J* = 4.03 Hz), 3.91 (t, 4H, *J* = 3.86 Hz), 4.58 (t, 4H, *J* = 3.82 Hz), 4.72 (m, 4H), 7.07 (d, 4H, *J* = 7.96 Hz), 7.49 (d, 4H, *J* = 8.06 Hz), 7.50 (m, 2H), 7.63 (t, 2H, *J* = 7.71 Hz), 7.96−8.06 (d, 2H, *J* = 8.18 Hz; d, 2H, *J* = 8.25 Hz), 9.39 (s, 2H); ^{13}C NMR (DMSO-*d*$_6$) δ 20.9, 46.3, 46.7, 67.6, 67.7, 69.7, 113.6, 113.9, 125.6, 126.5, 128.2, 130.9, 131.2, 137.5, 142.5, 145.7; MS (relative intensity) *m*/*z* 593 (M − TosO$^-$, 41.4%), 513 (M − TosO$^-$ − SO$_3$, 100%), 423 (M − 2TosO$^-$ − H$^+$); HRMS calcd for $C_{31}H_{37}N_4O_6S$ 593.2434, found 593.2437. Anal. Calcd for $C_{38}H_{44}N_4O_9S_2$: C, 59.67; H, 5.80. Found: C, 59.70; H, 6.00.

1,1′-Tri(ethyleneglycol)-3,3′-tetra(ethyleneglycol)bis(benzimidazolium) Ditosylate (8g). The salts were purified by washing aqueous solution with CH_2Cl_2. Colorless, crystalline solid (65%); mp 50−70 °C; ^{1}H NMR (DMSO-*d*$_6$) δ 2.25 (s, 6H), 3.20 (br s, 4H), 3.36 (br s, 4H), 3.50 (br s, 4H), 3.78 (br s, 8H), 4.65 (br s, 8H), 7.08 (d, 4H, *J* = 6.80 Hz), 7.51 (d, 4H, *J* = 7.00 Hz), 7.65 (br s, 4H), 8.06 (br s, 4H), 9.58 (s, 2H); ^{13}C NMR (DMSO-*d*$_6$) δ 20.9, 46.6, 67.1, 67.3, 69.4, 69.5, 69.6, 113.9, 125.6, 126.6, 128.2, 131.0, 131.0, 137.9, 143.0, 145.7; MS (relative intensity) *m*/*z* 681 (M − TosO$^-$, 85%), 509 (M − 2TosO$^-$ − H$^+$), 145 (100%); HRMS calcd for $C_{35}H_{45}N_4O_8S$ 681.2958, found 681.2958. Anal. Calcd for $C_{42}H_{52}N_4O_{11}S_2$: C, 59.14; H, 6.14. Found: C, 58.88; H, 5.94.

1,1′:3,3′-Bis(di(ethyleneglycol))bis(5,6-dimethylbenzimidazolium) Ditosylate (8h). The salts were purified by recrystallization. Colorless needles (83%); mp 238−239 °C; ^{1}H NMR (DMSO-*d*$_6$) δ 2.28 (s, 6H), 2.36 (s, 12H), 3.91 (br s, 8H), 4.62 (br s, 8H), 7.11 (d, 4H, *J* = 7.69 Hz), 7.50 (d, 4H, *J* = 7.81 Hz), 7.82 (s, 4H), 9.57 (s, 2H); ^{13}C NMR (DMSO-*d*$_6$) δ 20.0, 20.9, 46.9, 66.9, 113.2, 125.6, 128.2, 129.3, 136.3, 137.8, 141.7, 145.8. MS: no signals detected. Anal. Calcd for $C_{40}H_{48}N_4O_8S_2\cdot CH_3NO_2$: C, 58.76; H, 6.13. Found: C, 59.01; H, 5.99.

1,1′-Di(ethyleneglycol)-3,3′-tri(ethyleneglycol)bis(5,6-dimethylbenzimidazolium) Ditosylate (8i). The salts were purified by treatment of ethanolic solution with activated charcoal. Hard, yellowish resin (87%); ^{1}H NMR (DMSO-d_6) δ 2.24 (s, 6H), 2.31 (s, 6H), 2.39 (s, 6H), 3.43 (s, 4H), 3.79 (br s, 4H), 3.89 (br s, 4H), 4.53 (br s, 4H), 4.64 (br s, 4H), 7.06 (d, 4H, $J = 7.97$ Hz), 7.49 (d, 4H, $J = 7.73$ Hz), 7.79 (s, 2H), 7.85 (s, 2H), 9.21 (s, 2H); ^{13}C NMR (DMSO-d_6) δ 20.1, 20.9, 46.2, 46.7, 67.3, 67.8, 69.8, 113.2, 113.4, 125.6, 128.2, 129.4, 129.7, 136.4, 138.0, 141.3, 145.6; HRMS calcd for $C_{28}H_{38}N_4O_3$ 478.2944, found 478.2576. Anal. Calcd for $C_{42}H_{52}N_4O_9S_2 \cdot H_2O$: C, 60.12; H, 6.49. Found: C, 59.81; H, 6.48.

1,1′:3,3′-Bis(di(ethyleneglycol))bis(5-methylbenzimidazolium) Ditosylate (8j). The ether was obtained as a mixture of two isomers. The salts were purified by recrystallization. Colorless, fine crystals (54%); mp 270−285 °C; ^{1}H NMR (DMSO-d_6) δ 2.28 (s, 6H), 2.49 (s, 6H), 3.92 (br s, 8H), 4.65 (br s, 8H), 7.10 (d, 4H, $J = 7.73$ Hz), 7.40−7.51 (m, 6H), 7.85−7.95 (m, 4H), 9.65 (s, 2H); ^{13}C NMR (DMSO-d_6) δ 20.9, 21.3, 47.0, 47.0, 66.9, 113.1, 113.3, 125.6, 128.1, 128.2, 129.0, 131.1, 137.0, 137.8, 142.4, 145.8. MS: no signals detected. Anal. Calcd for $C_{38}H_{44}N_4O_8S_2$: C, 60.94; H, 5.92. Found: C, 61.07; H, 5.93.

1,1′:3,3′-Bis(di(ethyleneglycol))bis(5-methoxybenzimidazolium) Ditosylate (8k). The ether was obtained as a mixture of two isomers. The salts were purified by recrystallization. Light, tan-colored solid (94%); mp 256−268 °C (dec); ^{1}H NMR (DMSO-d_6) δ 2.27 (s, 6H), 3.86 (s, 6H), 3.92 (br s, 8H), 4.64 (br s, 8H), 7.09 (d, 4H, $J = 7.84$ Hz), 7.22 (d, 2H, $J = 9.89$ Hz), 7.49 (d, 4H, $J = 7.57$ Hz), 7.59 (s, 2H), 7.92 (d, 2H, $J = 9.64$ Hz), 9.60 (s, 2H); ^{13}C NMR (DMSO-d_6) δ 20.9, 46.9, 47.1, 56.4, 67.0 (br), 96.2, 114.5, 116.6, 125.1, 125.6, 128.2, 132.1, 137.8, 142.1, 145.7, 158.9. Anal. Calcd for $C_{38}H_{44}N_4O_{10}S_2$: C, 58.45; H, 5.68. Found: C, 58.60; H, 5.72.

1,1′:3,3′-Bis(di(ethyleneglycol))bis(5-chlorobenzimidazolium) Ditosylate (8l). The ether was obtained as a mixture of two isomers. The salts were purified by washing aqueous solution with CH_2Cl_2. Tan, hard resin (87%); mp 115−125 °C; ^{1}H NMR (DMSO-d_6) δ 2.27 (s, 6H), 3.92 (br s, 8H), 4.67 (br s, 8H), 7.08 (d, 4H, $J = 7.34$ Hz), 7.48 (d, 4H, $J = 7.57$ Hz), 7.65 (d, 2H, $J = 8.92$ Hz), 8.08 (d, 2H, $J = 8.93$ Hz), 8.29 (s, 2H), 9.79 (s, 2H); ^{13}C NMR (DMSO-d_6) δ 20.9, 47.3 (br), 66.9 (br), 113.8, 115.4 (br), 125.5, 127.0, 128.2, 129.8, 131.5, 131.7, 137.9, 144.1, 145.6. Anal. Calcd for $C_{36}H_{38}Cl_2N_4O_8S_2$: C, 54.75; H, 4.85. Found: C, 54.92; H, 5.02.

1,1′:3,3′-Bis(di(ethyleneglycol))bis(5-(trifluoromethyl)-benzimidazolium) Ditosylate (8m). The ether was obtained as a mixture of two isomers. The salts were purified by washing aqueous solution with CH_2Cl_2. Pale red solid (54%); mp 200−220 °C (dec); ^{1}H NMR (DMSO-d_6) δ 2.26 (s, 6H), 3.96 (br s, 8H), 4.77 (br s, 8H), 7.06 (d, 4H, $J = 7.70$ Hz), 7.46 (d, 4H, $J = 7.91$ Hz), 7.96 (d, 2H, $J = 8.53$ Hz), 8.31 (d, 2H, $J = 8.79$ Hz), 8.64 (s, 2H), 9.95 (s, 2H). Anal. Calcd $C_{38}H_{38}F_6N_4O_8S_2$: C, 53.27; H, 4.47. Found: C, 53.67; H, 4.62.

1,1′:3,3′-Bis(di(ethyleneglycol))bis(5-nitrobenzimidazolium) Ditosylate (8n). Mixture of two isomers. The salts were purified by washing crude material with CH_2Cl_2. Cream-colored powder (87%); mp 204−218 °C; ^{1}H NMR (DMSO-d_6) δ 2.25 (s, 6H), 3.98 (br s, 8H), 4.74 (br s, 4H), 4.80 (br s, 4H), 7.04 (d, 4H, $J = 7.67$ Hz), 7.41 (d, 4H, $J = 7.72$ Hz), 8.27 (d, 2H, $J = 9.06$ Hz), 8.36 (d, 2H, $J = 8.90$ Hz), 9.05 (s, 2H), 9.98 (s, 2H); ^{13}C NMR (DMSO-d_6) δ 20.8, 47.6, 66.9, 67.1, 110.9, 111.0, 115.0, 121.5, 125.5, 128.2, 130.8, 134.7, 137.9, 145.4, 145.7, 147.0. MS: no signals detected. Anal. Calcd for $C_{36}H_{38}N_6O_{12}S_2$: C, 53.32; H, 4.72. Found: C, 53.12; H, 4.59.

1,1′-Di(ethyleneglycol)-3,3′-di(ethylenethiogylcol)bis-(benzimidazolium) Ditosylate (8o). The salts were purified by recrystallization. Straw-colored crystals (75%); mp >200 °C; ^{1}H NMR (DMSO-d_6) δ 2.28 (s, 6H), 3.33 (br s, 4H), 4.01 (br s, 4H), 4.43 (s, CH_3NO_2), 4.73 (m, 8H), 7.10 (d, 4H, $J = 7.85$ Hz), 7.48 (d, 4H, $J = 8.24$ Hz), 7.62−7.65 (m, 4H), 8.04−8.07 (m, 4H), 9.85 (s, 2H); ^{13}C NMR (DMSO-d_6) δ 20.9, 30.2, 45.5, 47.2, 63.5 (CH_3NO_2), 67.5, 113.8, 125.6, 126.8, 128.2, 130.8, 131.1, 137.8, 142.7, 145.8; MS (relative intensity) *m/z* 565 (M − TosO$^-$, 100%), 394 (M − 2TosO$^-$); HRMS calcd for $C_{29}H_{33}N_4O_4S_2$ 565.1943, found 565.1970. Anal. Calcd for $C_{36}H_{40}N_4O_7S_3 \cdot 0.75\ CH_3NO_2$: C, 56.39; H, 5.44; N, 8.50. Found: C, 56.78; H, 5.42; N, 8.86.

1,1′:3,3′-Bis(1″,2″-bis(2‴-ethoxy)phenyl)bis(benzimidazolium) Ditosylate (8p). The salts were purified by treatment with cold nitromethane, followed by hot ethanol. Colorless, fine-crystalline solid (60%); mp 321.0−322.5 °C (dec); ^{1}H NMR (DMSO-d_6, low solubility) δ 2.26 (br s, 6H), 4.42 (br s, 8H), 4.90 (br s, 8H), 6.88 and 6.93 (br s, br s, 8H), 7.08 (br s, 4H), 7.47 and 7.54 (br s, br s, 8H), 8.09 (br s, 4H), 9.54 (br s, 2H); ^{13}C NMR (DMSO-d_6) δ 20.9, 46.7, 66.5, 114.0, 114.9, 122.2, 125.6, 126.7, 128.2, 131.2, 137.7, 142.6, 147.5; MS (relative intensity) *m/z* 733 (M − TosO$^-$, 100%), 561 (M − 2TosO$^-$ − 1); HRMS calcd for $C_{41}H_{41}N_4O_7S$ 733.2696, found 733.2738. Anal. Calcd for $C_{48}H_{48}N_4O_{10}S_2$: C, 63.70; H, 5.35. Found: C, 63.93; H, 5.33.

1,1′:3,3′-Bis(2″,3″-bis(2‴-ethoxy)naphthyl)bis(benzimidazolium) Ditosylate (8q). The salts were purified by treatment with hot ethanol. Off-white, microcrystalline solid (68%); mp 314−316 °C (dec); ^{1}H NMR (DMSO-d_6, low solubility) δ 2.22 (br s, 6H), 4.60 (br s, 8H), 5.03 (br s, 8H), 7.05 (d, 4H, $J = 7.96$ Hz), 7.30−7.40 (m, 8H), 7.47−7.55 (d, $J = 7.71$ Hz, m, 8H), 7.66−7.70 (m, 4H), 8.12−8.16 (m, 4H), 9.58 (br s, 2H); ^{13}C NMR (DMSO-d_6) δ 20.9, 46.7, 66.3, 109.1, 114.1, 124.6, 125.6, 126.5, 126.6, 128.1, 129.1, 131.3, 137.8, 142.5, 145.9, 147.4; MS (relative intensity) *m/z* 833 (M − TosO$^-$, 39%), 661 (M − 2TosO$^-$ − 1), 331 (cation/2, 100%). Anal. Calcd for $C_{56}H_{52}N_4O_{10}S_2$: C, 66.91; H, 5.21. Found: C, 67.02; H, 5.32.

1,1′-Di(ethyleneglycol)-3,3′-(α,α′-*o*-xylyl)bis(benzimidazolium) Ditosylate (8r). The salts were purified by filtration of hot aqueous solution, followed by recrystallization (CH_3NO_2). Fine, colorless needles (54%); mp 264−268 °C; ^{1}H NMR (DMSO-d_6) δ 2.27 (s, 6H), 3.68 (br s, 4H), 4.54 (br s, 4H), 5.83 (br s, 4H), 7.08 (d, 4H, $J = 7.81$ Hz), 7.40−7.55 (d, $J = 7.63$ Hz, m, 8H), 7.74−7.87 (d, $J = 8.45$ Hz, m, 6H), 8.12 (d, 2H, $J = 8.08$ Hz), 8.97 (s, 2H); ^{13}C NMR (DMSO-d_6) δ 20.9, 46.6, 47.6, 65.9, 113.5, 113.8, 125.6, 126.7, 126.7, 128.2, 130.2, 131.31, 131.34, 131.8, 134.2, 137.8, 141.7, 145.9; MS (relative intensity) *m/z* 581 (M − TosO$^-$, 23%), 409 (M − 2TosO$^-$ − 1, 100%); HRMS calcd for $C_{33}H_{33}N_4O_4S$ 581.2223, found 581.2129. Anal. Calcd for $C_{40}H_{40}N_4O_7S_2$: C, 63.81; H, 5.35. Found: C, 63.60; H, 5.52.

1,1′:3,3′-Bis(α,α′-*o*-xylyl)bis(benzimidazolium) Dibromide (8s).[15b] Colorless, fine-crystalline solid (82%); mp >275 °C (dec) (lit. >300 °C (dec)); ^{1}H NMR (DMSO-d_6, low solubility) δ 5.3−5.8 (br s, 4H), 5.9−6.4 (br s, 4H), 6.6−6.8 (shoulder, 2H), 6.8−7.3 (br s, 4H), 7.8 (br s, 5H), 7.9−8.3 (br s, 5H), 9.1−9.4 (br s, 2H). Mixture of two isomers. All peaks are broad: due to the small ring size of the macrocyclic ring, the benzimidazolium rings can point in the same or the opposite directions; ^{13}C NMR (DMSO-d_6) δ 49 (br), 113.8, 126.7, 130.1, 131.3, 132.5, 134.8, 141.5; MS (relative intensity) *m/z* 523, 521 (M − Br$^-$, 3.1%), 441 (M − 2 Br$^-$- 1, 100%); HRMS calcd for $C_{30}H_{26}BrN_4$ 521.1341, found 521.1306.

Preparation of Dibenzotetraaza (DBTA) Crown Ether 2: General Procedure. The procedure was adapted from ref 11. Powdered potassium hydroxide was added to a stirred solution of the appropriate bis(benzimidazolium) ditosylate (**8**) in an ethanol−*n*-propanol mixture, *n*-propanol, or *n*-amyl alcohol. The reaction was heated to 110 or 130 °C for 0.5 to 2 h. After cooling to room temperature, solid crown ethers were collected by filtration, rinsed with water (until pH = 7), and recrystallized. Oily products were purified by extraction, followed by column chromatography.

DBTA-18-Crown-6 (2a).[11] Potassium hydroxide (18 g) and ditosylate **8a** (10 g, 13.9 mmol) in 100 mL of *n*-propanol were heated to 110 °C for 1.5 h. The crude product was collected by filtration and then recrystallized from *n*-propanol. Colorless to straw-colored needles (79%); mp 185−188 °C (lit. 185.5−188.0 °C);[11] ^{1}H NMR ($CDCl_3$) δ 3.30 (t, 8H, $J = 4.62$ Hz), 3.57

(br s, 4H), 3.82 (t, 8H, $J = 4.46$ Hz), 6.62–6.66 (m, 4H), 6.78–6.82 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 43.5, 69.3, 110.5, 118.9, 136.9; MS (relative intensity) *m/z* 356 (M^+, 100%); HRMS calcd for $C_{20}H_{28}N_4O_2$ 356.2212, found 356.2222.

DBTA-24-Crown-8 (2b). Potassium hydroxide (0.65 g) and ditosylate **8b** (0.280 g, 0.35 mmol) in 3 mL of *n*-propanol were heated to 110 °C for 1.25 h. After cooling and addition of water, the crude product was collected by filtration and then recrystallized from *n*-propanol. Colorless, fine needles (80%); mp 124–125 °C; ^{1}H NMR ($CDCl_3$) δ 3.28 (t, 8H, $J = 4.81$ Hz), 3.66 (s, 8H), 3.78 (t, 8H, $J = 4.93$ Hz), 3.96 (br s, 4H), 6.65–6.68 (m, 4H), 6.76–6.79 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 44.0, 69.6, 70.1, 112.0, 119.1, 137.4; MS (relative intensity) *m/z* 444 (M^+, 76.4%), 429 (100%); HRMS calcd for $C_{24}H_{36}N_4O_4$ 444.2737, found 444.2727. Anal. Calcd for $C_{24}H_{36}N_4O_4$: C, 64.84; H, 8.16; N, 12.60. Found: C, 65.03; H, 8.15; N, 12.70.

DBTA-30-Crown-10 (2c). Potassium hydroxide (1.10 g) and ditosylate **8c** (0.63 g, 0.70 mmol) in 20 mL of *n*-propanol were heated to 110 °C for 2 h. After cooling and addition of water, the crude product was collected by filtration and then recrystallized from ethanol (95%). Off-white, fine amorphous solid (43%); mp 110.5–111.5 °C; ^{1}H NMR ($CDCl_3$) δ 3.26 (t, 8H, $J = 4.85$ Hz), 3.68 (br s, 16H), 3.75 (t, 8H, $J = 5.19$ Hz), 3.83 (br s, 4H), 6.61–6.66 (m, 4H), 6.74–6.80 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 43.9, 69.8, 70.5, 70.6, 111.6, 119.0, 137.3; MS (relative intensity) *m/z* 532 (M^+, 54.1%), 517 (100%); HRMS calcd for $C_{28}H_{44}N_4O_6$ 532.3261, found 532.3258. Anal. Calcd for $C_{28}H_{44}N_4O_6$: C, 63.13; H, 8.33; N, 10.52. Found: C; 63.00; H, 8.12; N, 10.33.

DBTA-36-Crown-12 (2d). Potassium hydroxide (0.75 g) and ditosylate **8d** (0.37 g, 0.376 mmol) in ethanol–*n*-propanol 2:1 were heated to 110 °C for 1.5 h. After cooling and the addition of water, the product was isolated by extraction with ether. No further purification was necessary. Colorless oil (82%); ^{1}H NMR ($CDCl_3$) δ 3.27 (t, 8H, $J = 4.42$ Hz), 3.55–3.70 (m, 24H), 3.76 (t, 8H, $J = 5.12$ Hz), 6.61–6.68 (m, 4H), 6.73–6.79 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 44.0, 69.8, 70.4, 70.6, 70.7, 111.8, 119.1, 137.3; MS (relative intensity) *m/z* 621 ($M^+ + 1$, 100%); HRMS calcd for $C_{32}H_{53}N_4O_8$ 621.3863, found 621.3539. Anal. Calcd for $C_{32}H_{52}N_4O_8$ C, 61.91; H, 8.44; N, 9.03. Found: C, 62.15; H, 8.27; N, 9.28.

DBTA-42-Crown-14 (2e). Potassium hydroxide (0.70 g) and ditosylate **8e** (0.40 g, 0.373 mmol) in ethanol–*n*-propanol 2:1 were heated to 110 °C for 2 h. After cooling and the addition of water, the product was isolated by extraction with ether. No further purification was necessary. Colorless oil (76%); ^{1}H NMR ($CDCl_3$) δ 3.27 (t, 8H, $J = 5.17$ Hz), 3.65 (br s, 32H), 3.74 (t, 8H, $J = 5.15$ Hz), 6.62–6.68 (m, 4H), 6.72–6.79 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 44.0, 69.8, 70.3, 70.7 (br), 111.8, 119.1, 137.3; MS (relative intensity) *m/z* 709 ($M^+ + 1$, 100%). HRMS calcd for $C_{36}H_{61}N_4O_{10}$ 709.4388, found 709.4388. Anal. Calcd for $C_{36}H_{60}N_4O_{10}$: C, 61.00; H, 8.53; N, 7.90. Found: C, 61.21; H, 8.45; N, 8.03.

DBTA-21-Crown-7 (2f). Potassium hydroxide (1.10 g) and ditosylate **8f** (0.55 g, 0.719 mmol) in ethanol–*n*-propanol 3:1 were heated to 110 °C for 2 h. After cooling and addition of water, the crude product was collected by filtration and then recrystallized from ethanol (95%). Grayish, fine needles (57%); mp 122–123 °C; ^{1}H NMR ($CDCl_3$) δ 3.29 (t, 8H, $J = 4.25$ Hz), 3.66 (s, 4H), 3.70–3.85 (m, 12H), 6.60–6.70 (m, 4H), 6.70–6.80 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 44.2, 44.6, 70.0, 70.6, 111.6, 111.8, 119.0 (br), 137.2, 137.3; MS (relative intensity) *m/z* 400 (M^+, 76.2%), 385 (100%); HRMS calcd for $C_{22}H_{32}N_4O_3$ 400.2474, found 400.2491 (M^+). Anal. Calcd for $C_{22}H_{32}N_4O_3$: C, 65.97; H, 8.05. Found: C, 66.12; H, 8.20.

DBTA-27-Crown-9 (2g). Potassium hydroxide (1.00 g) and ditosylate **8g** (0.53 g, 0.621 mmol) in ethanol–*n*-propanol 3:1 were heated to 110 °C for 2 h. After cooling and the addition of water, the product was extracted with chloroform. The product was purified by column chromatography (SiO_2; CH_2Cl_2/ethanol 95:5). Pale yellow oil (37%); ^{1}H NMR ($CDCl_3$) δ 3.20–3.27 (m, 8H), 3.64 (br s, 12H), 3.69–3.79 (m, 8H), 6.58–6.68 (m, 4H), 6.71–6.78 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 43.9, 69.7, 69.8, 70.2, 70.4, 70.5, 111.8, 119.0, 119.1, 137.2, 137.4; MS (relative intensity) *m/z* 489 ($M^+ + 1$, 39.6%), 161 (100%); HRMS calcd for $C_{26}H_{41}N_4O_5$ 489.3077, found 489.3213. Anal. Calcd for $C_{26}H_{40}N_4O_5$: C, 63.91; H, 8.25; N, 11.47. Found: C; 64.08; H, 8.07; N, 11.42.

Tetramethyl DBTA-18-Crown-6 (2h). Potassium hydroxide (1.75 g) and ditosylate ($\cdot CH_3NO_2$) **8h** (0.215 g, 0.26 mmol) in *n*-amyl alcohol (5 mL) were heated to 130 °C for 2 h. Ethanol (5 mL) was added, and stirring was continued for an additional 0.5 h. After cooling and the addition of water, the product was isolated by extraction with ether with inclusion of any undissolved solid, followed by treatment with hot *n*-amyl alcohol. Colorless, fine powder (69%); mp 225–226 °C; ^{1}H NMR ($CDCl_3$) δ 2.19 (s, 12H), 3.28 (t, 8H, $J = 4.01$ Hz), 3.56 (br s, 4H), 3.79 (t, 8H, $J = 4.34$ Hz), 6.43 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 19.2, 43.8, 69.4, 112.7, 126.0, 134.9; MS (relative intensity) *m/z* 412 (M^+, 89%), 397 (100%); HRMS calcd for $C_{24}H_{36}N_4O_2$ 412.2838, found 412.2849. Anal. Calcd for $C_{24}H_{36}N_4O_2$: C, 69.87; H, 8.80; N, 13.58. Found: C, 70.02; H, 8.63; N, 13.49.

Tetramethyl DBTA-21-Crown-7 (2i). Potassium hydroxide (1.75 g) and ditosylate ($\cdot H_2O$) **8i** (200 mg, 0.238 mmol) in *n*-amyl alcohol (5 mL) were heated to 130 °C for 0.5 h. Ethanol (5 mL) was added, and stirring was continued for an additional few minutes. After cooling and the addition of water, the product was isolated by extraction with ether. After removal of the solvent, the crude product was washed with ice cold methanol (1 mL). The solid was further purified by column chromatography (Al_2O_3; C_6H_6). Colorless solid (37%); mp 154.0–154.5 °C; ^{1}H NMR ($CDCl_3$) δ 2.16 (s, 12H), 3.20–3.30 (m, 8H), 3.67 (s, 4H), 3.73 (t, 8H, $J = 4.56$ Hz), 3.82 (br s, 4H), 6.46 (s, 2H), 6.48 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 19.2, 45.0, 45.1, 69.9, 70.0, 70.6, 114.8, 115.3, 126.6, 127.0, 135.3, 135.9; MS (relative intensity) *m/z* 456 (M^+, 83%), 441 (100%); HRMS calcd for $C_{26}H_{40}N_4O_3$ 456.3100, found 456.3099. Anal. Calcd for $C_{26}H_{40}N_4O_3$: C, 68.39; H, 8.83; N, 12.27. Found: C, 68.50; H, 8.78; N, 12.12.

Dimethyl DBTA-18-Crown-6 (2j). The ether was obtained as a mixture of two isomers. Potassium hydroxide (4.4 g) and ditosylate **8j** (0.50 g, 0.67 mmol) in *n*-amyl alcohol were heated to 130 °C for 1 h. After cooling and the addition of water, the product was isolated by extraction with ether. The crude product was purified by column chromatography (Al_2O_3 (neutral); C_6H_6 then C_6H_6–ether 1:1), followed by treatment with hot ethanol. Colorless powder (50%); mp 188.5–189.5 °C; ^{1}H NMR ($CDCl_3$) δ 2.27 (s, 6H), 3.26–3.32 (m, 8H), 3.64 (br s, 4H), 3.81 (t, 8H, $J = 4.31$ Hz), 6.46 (s, 2H), 6.52–6.61 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 21.1, 43.5, 43.8, 69.3, 69.4, 110.7, 111.5, 118.8, 128.4, 134.4, 137.2; MS (relative intensity) *m/z* 384 (M^+, 83%), 133 (100%); HRMS calcd for $C_{22}H_{32}N_4O_2$ 384.2525, found 384.2545. Anal. Calcd for $C_{22}H_{32}N_4O_2$: C, 68.72; H, 8.39; N, 14.57. Found: C, 68.73; H, 8.45; N, 14.34.

Dimethoxy DBTA-18-Crown-6 (2k). The ether was obtained as a mixture of two isomers. Potassium hydroxide (2.5 g) and ditosylate **8k** (300 mg, 0.384 mmol) in *n*-amyl alcohol were heated to 130 °C for 45 min. After cooling and the addition of water, the product was isolated by extraction with ether. The crude product was purified by column chromatography (Al_2O_3 (neutral); C_6H_6 then C_6H_6–ether 1:1), followed by recrystallization from ethanol. Colorless solid (46%); mp 160 °C; ^{1}H NMR ($CDCl_3$) δ 3.24–3.30 (m, 8H), 3.76 (s, 6H), 3.78 (m, 8H), 6.26–6.30 (m, 4H), 6.56 (d, 2H, $J = 8.05$ Hz); ^{13}C NMR ($CDCl_3$) δ 43.4, 44.2, 55.5, 69.1, 69.5, 99.0, 100.7, 111.5, 130.6, 139.1, 154.0; MS (relative intensity) *m/z* 416 (M^+, 100%); HRMS calcd for $C_{22}H_{32}N_4O_4$ 416.2424, found 416.2411. Anal. Calcd for $C_{22}H_{32}N_4O_4$: C, 63.44; H, 7.74; N, 13.45. Found: C, 63.40; H, 7.63; N, 13.21.

Dichloro DBTA-18-Crown-6 (2l). The ether was obtained as a mixture of two isomers. Potassium hydroxide (0.75 g) and ditosylate **8l** (208 mg, 0.263 mmol) in *n*-propanol were heated to 130 °C for 30 min. After cooling, the product was isolated by filtration. The crude material was washed with water and purified by column chromatography (Al_2O_3 (neutral); C_6H_6 then C_6H_6−ether 1:1), followed by treatment with refluxing methanol. Colorless powder (55%); mp 205−209 °C (dec); ^{1}H NMR ($CDCl_3$) δ 3.26 (t, 8H, J = 4.55 Hz), 3.65 (br s, 4H), 3.81 (t, 8H, J = 4.64 Hz), 6.49−6.58 (m, 4H), 6.71−6.75 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 43.4, 43.6, 69.0, 69.2, 110.6, 111.3, 118.1, 124.3, 135.3, 138.1; MS (relative intensity) m/z 428, 426, 424 (M^+, 70%), 153 (100%); HRMS calcd for $C_{20}H_{26}Cl_2N_4O_2$ 424.1433, found 424.1432. Anal. Calcd for $C_{20}H_{26}Cl_2N_4O_2$: C, 56.47; H, 6.16; N, 13.17. Found: C, 56.70; H, 6.24; N, 12.99.

Di(trifluoromethyl) DBTA-18-Crown-6 (2m). The ether was obtained as a mixture of two isomers. Potassium hydroxide (0.90 g) and ditosylate **8m** (260 mg, 0.304 mmol) in ethanol were heated to 100 °C for 15 min. After cooling and the addition of water, the product was isolated by extraction with ether. The crude product was purified by flash column chromatography (Al_2O_3 (basic); ether). Lightly reddish solid (41%); mp ~55−65 °C; ^{1}H NMR ($CDCl_3$) δ 3.33 (br s, 8H), 3.7 (br s, 4H), 3.84 (br s, 8H), 6.58 (d, 2H, J = 8.39 Hz), 6.85 and 6.86 (s, s, 2H), 7.07 (d, 2H, J = 7.04 Hz). The compound decomposed slowly in solution.

Dinitro DBTA-18-Crown-6 (2n). The ether was obtained as a mixture of two isomers. Ditosylate **8n** (230 mg, 0.284 mmol) was dissolved in refluxing ethanol (25 mL, ~0.5 h), and the mixture was chilled to −5−0 °C. Potassium hydroxide (3.5 g) was added, and the mixture was stirred at −5−0 °C. The mixture turned deep red immediately. TLC (Al_2O_3; CH_2Cl_2−ethanol 95:5) showed one yellow spot (R_f = 0.63) attributed to the diformamide **15**. After an additional 3.5 h at 0 °C, TLC showed an additional spot of equal intensity (R_f = 0.85, orange, attributed to **2n**). After the mixture was stirred at room temperature for 1.25 h, TLC showed only the orange spot at R_f = 0.85 (**2n**). Water was added, and the mixture was extracted with chloroform. After washing and drying, a bright yellow solution was obtained. Removal of the solvent yielded a small amount of a powdery orange-red solid. An NMR ($CDCl_3$; low solubility) of the crude compound indicated the presence of the product. Column chromatography (basic Al_2O_3; $CHCl_3$) afforded a yellow-orange solid together with unidentified impurities. Yellow-orange solid; ^{1}H NMR ($CDCl_3$) δ 3.39 (m, 8H), 3.5−4.0 (br s, 4H), 3.87 (br s, 8H), 6.57 (d, 2H, J = 8.77 Hz), 7.53 and 7.54 (s, s, 2H), 7.84 (d, 2H, J = 9.38 Hz). Only signals attributed to **2n** are listed.

Diamino DBTA-18-Crown-6 (2o). The ether was obtained as a mixture of two isomers. The crude reaction mixture containing **2n** was neutralized with ice-cold 3 N HCl_{aq} at 0 °C. The pH was adjusted to ~7 by the addition of saturated aqueous $NaHCO_3$ solution. $Na_2S_2O_4$ (3 g) was added, and the reaction mixture was heated to 90 °C. After 7 min, another 6 g of $Na_2S_2O_4$ was added and the temperature was increased to 110 °C. The color of the mixture began to fade to a light yellow-orange and then to nearly colorless (~5 to 7 min). After an additional 5 min, another 3 g of $Na_2S_2O_4$ was added, followed by 10 min of heating. TLC (Al_2O_3; CH_2Cl_2/ethanol 95:5) showed *one* moving spot (R_f = 0.58) attributed to **2o**. Ethanol was removed under reduced pressure, and water was added. Extraction with chloroform yielded a sand-colored solid. NMR spectra showed essentially pure **2o**. The compound appeared to be stable as a solid, but it decomposed during the acquisition of the NMR spectra in solution. Cream-colored solid (14%, from **8n**); ^{1}H NMR ($CDCl_3$) δ 3.20−3.27 (m, 8H), 2.8−3.6 (br s, ~8H, −NH and −NH_2), 3.78 (br s, 8H), 6.06 (s, 2H), 6.12 (d, 2H, J = 8.32 Hz), 6.49 (d, 2H, J = 8.20 Hz); ^{13}C NMR ($CDCl_3$) δ 43.4, 44.3, 69.2, 69.7, 99.7, 104.6, 112.6.

DBTA Oxathia-18-Crown-6 (2p). Potassium hydroxide (1.0 g) and ditosylate **8o** (0.30 g, 0.38 mmol) in n-propanol were heated to 110 °C for 1.5 h. After cooling, the solution was diluted with methanol. The crude product was collected by filtration and then purified by rinsing with methanol and water. Colorless, microcrystalline solid (78%); mp 168−169 °C; ^{1}H NMR ($CDCl_3$) δ 2.98 (t, 4H, J = 5.62 Hz), 3.29−3.37 (m, 8H), 3.7−3.9 (br s, 4H), 3.83 (t, 4H, J = 4.58 Hz), 6.60−6.68 (m, 4H), 6.77−6.82 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 31.6, 41.6, 43.8, 69.8, 110.7, 111.1, 119.0, 119.2, 136.8, 136.9; MS (relative intensity) m/z 373 (M^+ + 1, 100%); HRMS calcd for $C_{20}H_{29}N_4OS$ 373.2062, found 373.4378. Anal. Calcd for $C_{20}H_{28}N_4OS$: C, 64.48; H, 7.58; N, 15.04. Found: C, 64.61; H, 7.50; N, 14.89.

Tetrabenzotetraaza-24-Crown-8 (2q). Ditosylate **8p** (0.70 g, 0.77 mmol) was dissolved in refluxing methanol (90 mL). The flask was removed from the heat, and 8 g of potassium hydroxide was added slowly. The solution was heated to reflux for 5 min. The flask was removed from the heat again, and n-butanol (90 mL) and potassium hydroxide (20 g) were added. At this point, a colorless precipitate formed. After 5 min of reflux, more potassium hydroxide (10 g) was added. Reflux was continued for 50 min. After cooling, the crude product was collected by filtration, rinsed with water, and heated in refluxing ethanol (95%). Colorless, microcrystalline solid (90%); mp 207.5−208.0 °C (dec); ^{1}H NMR (DMSO-d_6) δ 3.39 (br s, 8H), 4.19 (br s, 8H), 4.68 (br s, 4H), 6.54 and 6.57 (br s, br s, 8H), 6.89 (br s, 4H), 7.00 (br s, 4H); ^{13}C NMR (DMSO-d_6) δ 43.5, 69.8, 110.4, 114.5, 117.9, 121.4, 136.4, 148.6; MS (relative intensity) m/z 541 (M^+ + 1, 82%), 161 (100%); HRMS calcd for $C_{32}H_{37}N_4O_4$ 541.2815, found 541.2781. Anal. Calcd for $C_{32}H_{36}N_4O_4$: C, 71.09; H, 6.71; N, 10.36. Found: C, 71.23; H, 6.84; N, 10.19.

Dibenzodinaphthotetraaza-24-Crown-8 (2r). Ditosylate **8q** (0.20 g, 0.20 mmol) was dissolved in refluxing methanol (15 mL). The flask was removed from the heat, and potassium hydroxide (5 g) was added slowly. The solution was heated to reflux for 5 min. The flask was removed from the heat, and n-butanol (15 mL) and potassium hydroxide (5 g) were added. Reflux was continued for 1 h. After cooling, the crude product was collected by filtration, rinsed with water, and treated with three portions of DMSO (1 mL each) at 50 °C, followed by a methanol rinse. The product is nearly insoluble in common organic solvents. Colorless, fine powder (67%); mp 228−230 °C (dec); ^{1}H NMR (DMSO-d_6) δ 3.51 (br s, 8H), 4.35 (br s, 8H), 4.88 (br s), 6.50−6.65 (m, 8H), 7.20−7.34 (m, 4H), 7.36 (s, 4H), 7.65−7.75 (m, 4H); ^{13}C NMR (DMSO-d_6) no signals detected. Solubility was too low. MS: no signals detected. Anal. Calcd for $C_{40}H_{40}N_4O_4 \cdot 0.5\ C_2H_6SO$; C, 72.43; H, 6.38; N, 8.24. Found: C, 72.70; H, 6.00; N, 8.17.

Preparation of Bis(benzimidazolidine) Crown Ether 9: General Procedure. The procedure was adapted from ref 11. To a stirred solution of bis(benzimidazolium) ditosylate **8** in methanol an excess of $NaBH_4$ was added in small portions over several minutes. Stirring was continued for approximately 0.5 h. The product precipitated during this time or after the addition of water. It was collected by filtration and then rinsed with water (until pH = 7). In some cases, the product was refluxed with water or ethanol.

1,1′:3,3′-Bis(di(ethyleneglycol))bis(benzimidazolidine) (9a).[11] The reaction was carried out with 2.00 g (2.77 mmol) of ditosylate **8a** and 230 mg of $NaBH_4$. Colorless powder (77%); mp 137−140 °C (lit. 143.5−144.0 °C);[11] ^{1}H NMR ($CDCl_3$) δ 3.25 (t, 8H, J = 4.00 Hz), 3.70 (t, 8H, J = 4.07 Hz), 4.74 (s, 4H), 6.36 (m, 4H), 6.63 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 48.5, 72.0, 78.9, 105.5, 118.7, 141.8.

1,1′:3,3′-Bis(tri(ethyleneglycol))bis(benzimidazolidine) (9b). The reaction was carried out with 2.12 g (2.62 mmol) of ditosylate **8b** and 300 mg of $NaBH_4$. Colorless powder (82%); mp 123−127 °C; ^{1}H NMR ($CDCl_3$) δ 3.25 (t, 8H, J = 5.25 Hz), 3.62 (s, 8H), 3.70 (t, 8H, J = 5.38 Hz), 4.77 (s, 4H), 6.32−6.35 (m, 4H), 6.57−6.61 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 48.2, 70.0, 70.7, 78.0, 105.3, 118.5, 142.0; MS (relative intensity) m/z 467 (M^+ − 1, 100%); HRMS calcd for $C_{26}H_{36}N_4O_4$ 468.2737, found 468.2698. Anal. Calcd for $C_{26}H_{36}N_4O_4$: C, 66.64; H, 7.74. Found: C, 66.39; H, 7.56.

1,1′:3,3′-Bis(tetra(ethyleneglycol))bis(benzimidazolidine) (9c). The reaction was carried out with 2.99 g (3.33 mmol) of ditosylate **8c** and 500 mg of $NaBH_4$. Yellowish-gray crystals (40%); mp 86−94 °C; ^{1}H NMR ($CDCl_3$) δ 3.24 (t, 8H, J = 5.22 Hz), 3.63−3.72 (m, 24H), 4.70 (s, 4H), 6.33−

6.37 (m, 4H), 6.58−6.62 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 48.2, 70.1, 70.6, 77.9, 105.4, 118.6, 141.9; MS (relative intensity) *m/z* 555 ($M^+ - 1$, 100%); HRMS calcd for $C_{30}H_{44}N_4O_6$ 556.3261, found 556.3299. Anal. Calcd for $C_{30}H_{44}N_4O_6$: C, 64.73; H, 7.97. Found: C, 64.56; H, 7.86.

1,1′:3,3′-Bis(di(ethyleneglycol))bis(5,6-dimethylbenzimidazolidine) (9d). The reaction was carried out with 1.64 g (1.96 mmol) of ditosylate ($\cdot CH_3NO_2$) **8h** and 150 mg of $NaBH_4$. Colorless powder (82%); mp 182−184 °C (dec); ^{1}H NMR ($CDCl_3$) δ 2.13 (s, 12H), 3.20 (t, 8H, *J* = 3.73 Hz), 3.69 (t, 8H, *J* = 4.01 Hz), 4.59 (s, 4H), 6.22 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 19.5, 49.3, 72.2, 79.7, 108.3, 126.0, 140.2; MS (relative intensity) *m/z* 436 (M^+, 100%); HRMS calcd for $C_{26}H_{36}N_4O_2$ 436.2838, found 436.2849. Anal. Calcd for $C_{26}H_{36}N_4O_2$: C, 71.53; H, 8.31; N, 12.83. Found: C, 71.39; H, 8.27; N, 12.80.

1,1′-Di(ethyleneglycol)-3,3′-tri(ethyleneglycol)bis(5,6-dimethylbenzimidazolidine) (9e). The reaction was carried out with 1.50 g (1.79 mmol) of ditosylate ($\cdot H_2O$) **8i** and 150 mg of $NaBH_4$. Colorless powder (46%); mp 98−110 °C (dec); ^{1}H NMR ($CDCl_3$) δ 2.12 (s, 12H), 3.22 (t, 8H, *J* = 5.64 Hz), 3.62 (s, 4H), 3.67 (t, 4H, *J* = 4.80 Hz), 3.71 (t, 4H, *J* = 4.88 Hz), 4.68 (s, 4H), 6.16 and 6.18 (s, s, 2H); ^{13}C NMR ($CDCl_3$) δ 19.5, 48.9, 49.2, 70.8, 71.0, 79.2, 107.7, 107.9, 125.6, 140.2; MS (relative intensity) *m/z* 480 (M^+, 100%); HRMS calcd for $C_{28}H_{40}N_4O_3$ 480.3100, found 480.3106. Anal. Calcd for $C_{28}H_{40}N_4O_3$: C, 69.97; H, 8.39; N, 11.66. Found: C, 69.76; H, 8.17; N, 11.78.

1,1′:3,3′-Bis(di(ethyleneglycol))bis(5-(trifluoromethyl)-benzimidazolidine) and 1,1′:3,3′-Bis(di(ethyleneglycol))-(5-(trifluoromethyl)benzimidazolidine)(6′-(trifluoromethyl) benzimidazolidine) (9f). The ether was obtained as a mixture of two isomers. The reaction was carried out with 0.10 g (0.117 mmol) of ditosylate **8m** and 100 mg of $NaBH_4$. Pale red powder (91%); mp >100 °C (dec); ^{1}H NMR ($CDCl_3$) δ 3.28−3.33 (m, 8H), 3.67−3.70 (m, 8H), 4.96 (s, 4H), 6.22 (d, 2H, *J* = 7.71 Hz), 6.39 (s, 2H), 6.86 (d, 2H, *J* = 7.85 Hz); ^{13}C NMR ($CDCl_3$) δ 47.2, 47.6, 71.3, 71.4, 78.1, 100.4, 102.7, 141.8, 144.3; MS (relative intensity) *m/z* 515, 514, 513 ($M^+ - 3$, 100%), 257 ($M^+/2{-}1$); HRMS calcd for $C_{24}H_{23}F_6N_4O_2$ 513.1725, found 513.1726.

1,1′:3,3′-Bis(di(ethyleneglycol))bis(5-nitrobenzimidazolidine) and 1,1′:3,3′-Bis(di(ethyleneglycol))(5-nitrobenzimidazolidine)(6′-nitrobenzimidazolidine) (9g). The ether was obtained as a mixture of two isomers. The reaction was carried out with 0.35 g (0.43 mmol) of ditosylate **8n** and 250 mg of $NaBH_4$. Brick red powder (91%); mp >155 °C (dec); ^{1}H NMR ($CDCl_3$) 3.39 (br s, 4H), 3.48 (br s, 4H), 3.62 (br s, 8H), 5.17 (s, 4H), 6.29 (d, 2H, *J* = 8.63 Hz), 6.90 (s, 2H), 7.54 (d, 2H, *J* = 8.80 Hz); ^{13}C NMR ($CDCl_3$) δ 44.8, 45.5, 69.6, 76.1, 96.1, 100.1, 118.6, 138.0, 141.4, 147.7; MS (relative intensity) *m/z* 471 ($M^+ + 1$, 16.4%), 469 ($M^+ - 1$, 99.1%), 289 (100%); HRMS calcd for $C_{22}H_{25}N_6O_6$ 469.1836, found 469.1829. Anal. Calcd for $C_{22}H_{26}N_6O_6$: C: 56.16; H, 5.57; N, 17.86. Found: C, 56.20; H, 5.33; N, 17.85.

1,1′-Di(ethyleneglycol)-3,3′-di(ethylenethioglycol)bis(benzimidazolidine) (9h). The reaction was carried out with 0.20 g (0.26 mmol) of ditosylate (0.75 $\cdot CH_3NO_2$) **8o** and 150 mg of $NaBH_4$. Colorless, fine powder (81%); mp 120−130 °C (dec); ^{1}H NMR ($CDCl_3$) δ 2.87 (t, 4H, *J* = 6.05 Hz), 3.24 (t, 4H, *J* = 4.19 Hz), 3.34 (t, 4H, *J* = 6.03 Hz), 3.70 (t, 4H, *J* = 4.40 Hz), 4.73 (s, 4H), 6.30−6.35 (m, 2H), 6.42−6.47 (m, 2H), 6.63−6.66 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 30.2, 47.7, 50.5, 70.4, 77.6, 105.1, 105.7, 118.8, 118.9, 141.6, 142.0; MS (relative intensity) *m/z* 396 (M^+, 100%); HRMS calcd for $C_{22}H_{28}N_4OS$ 396.1984, found 396.2007. Anal. Calcd for $C_{22}H_{28}N_4OS$: C, 66.63; H, 7.12; N, 14.13. Found: C, 66.50; H, 7.16; N, 13.89.

1,1′:3,3′-Bis(1″,2″-bis(2‴-ethoxy)phenyl)bis(benzimidazolidine) (9i). The reaction was carried out with 0.14 g (0.155 mmol) of ditosylate **8p** (dissolved in hot methanol then cooled to room temperature) and 140 mg of $NaBH_4$. The product was nearly insoluble in common organic solvents. Colorless powder (46%); mp 230−234 °C (dec). ^{1}H, ^{13}C NMR: no signals detected. Solubility too low. HRMS: no signals detected. Anal. Calcd for $C_{34}H_{36}N_4O_4 \cdot 0.2\ CHCl_3$: C, 69.79; H, 6.20; N, 9.52. Found: C, 69.64; H, 5.95; N, 9.28.

1,1′-Di(ethyleneglycol)-3,3′-(α,α′-*o*-xylyl)bis(benzimidazolidine) (9j). The reaction was carried out with 0.213 g (0.283 mmol) of ditosylate **8r** and 80 mg of $NaBH_4$. Colorless, microcrystalline solid (90%); mp 127−135 °C (dec); ^{1}H NMR ($CDCl_3$) δ 3.17 (t, 4H, *J* = 4.28 Hz), 3.57 (t, 4H, *J* = 4.26 Hz), 4.29 (s, 4H), 4.52 (s, 4H), 6.20−6.25 (m, 2H), 6.49−6.53 (m, 2H), 6.58−6.62 (m, 4H), 7.23−7.28 (m, 2H), 7.37−7.42 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 45.6, 47.8, 69.9, 75.1, 104.2, 104.9, 118.1, 118.7, 128.0, 130.7, 136.7, 141.2, 141.6; MS (relative intensity) *m/z* 411 ($M^+ - 1$, 100%); HRMS calcd for $C_{26}H_{27}N_4O$ 411.2185, found 411.2285. Anal. Calcd for $C_{26}H_{28}N_4O$: C, 75.70; H, 6.84; N, 13.58. Found: C, 75.61; H, 6.68; N, 13.56.

1,1′:3,3′-Bis(α,α′-*o*-xylyl)bis(benzimidazolidine) (9k). The reaction was carried out with 0.286 g (0.475 mmol) of dibromide **8s** and 85 mg of $NaBH_4$. Off-white, microcrystalline solid (82%); mp 170−172 °C (dec); ^{1}H NMR ($CDCl_3$) δ 3.92 (s, 4H), 4.16 (s, 8H), 6.59−6.63 (m, 4H), 6.72−7.76 (m, 4H), 7.19−7.24 (m, 4H), 7.39−7.42 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 50.9, 73.1, 108.8, 120.5, 128.0, 130.8, 136.0, 143.5; MS (relative intensity) *m/z* 444 (M^+, 30.3%), 104 (100%); HRMS calcd for $C_{30}H_{28}N_4$ 444.2314, found 444.2282. Anal. Calcd for $C_{30}H_{28}N_4 \cdot 0.95\ B(OH)_3$: C, 71.59; H, 6.18; N, 11.13. Found: C, 71.75; H, 5.88; N, 10.80.

Preparation of Tetra(*N*-organyl)dibenzotetraaza Crown Ether 10: General Procedure. The appropriate DBTA crown ether **2** (1 mmol), K_2CO_3 (15−20 mmol; dry and ground), and about 70−130 mmol of alkyl iodide (or benzyl chloride) were stirred well and heated gently. Details are listed in Table 3. The progress of the reaction was monitored by TLC (Al_2O_3, ether). The product had a higher R_f value than the starting material and the partially alkylated compounds. Toward the end of the reaction, 2-D TLC plates were run (Al_2O_3; first ether, then (at a 90° angle) C_6H_6). Partially alkylated crown ethers were indicated by shoulders next to the product. Reaction times varied depending on stirring, coarseness of K_2CO_3, and temperature. As soon as no partially alkylated crown ethers were detected, the excess halide was removed under a stream of Ar or under reduced pressure. The colorless residue was extracted with C_6H_6. The extracts were filtered through a short Al_2O_3 (basic) column, and the column was rinsed with C_6H_6. The product was initially obtained as resinous oil.

Tetra(*N*-methyl) DBTA-18-Crown-6 (10a). Colorless, crystalline solid (72%); mp 72−73 °C (lit. 72.5−73.5 °C);[13] ^{1}H NMR ($CDCl_3$) δ 2.72 (s, 12H), 3.33 (t, 8H, *J* = 6.10 Hz), 3.51 (t, 8H, *J* = 6.08 Hz), 6.88 (s, 8H); ^{13}C NMR ($CDCl_3$) δ 40.3, 52.9, 68.3, 119.2, 121.9, 145.5; MS (relative intensity) *m/z* 412 (M^+, 0.55%), 352 ($M^+ - 4Me$), 147 (100%); HRMS calcd for $C_{24}H_{37}N_4O_2$ 413.2917, found 413.2897; Anal. Calcd for $C_{24}H_{36}N_4O_2$: C, 69.87; H, 8.80; N, 13.58. Found: C, 70.07; H, 8.97; N, 13.74.

Tetra(*N*-ethyl) DBTA-18-Crown-6 (10b). Colorless, crystalline solid (82%); mp 102−103 °C; ^{1}H NMR ($CDCl_3$) δ 0.96 (t, 12H, *J* = 7.15 Hz), 3.18 (q, 8H, *J* = 7.15 Hz), 3.35 (br s, 16H), 6.83 (s, 8H); ^{13}C NMR ($CDCl_3$) δ 12.1, 45.6, 49.2, 67.9, 121.0, 121.4, 143.6; MS (relative intensity) *m/z* 468 (M^+, 45.5%), 175 (100%); HRMS calcd for $C_{28}H_{45}N_4O_2$ 469.3543, found 469.3572. Anal. Calcd for $C_{28}H_{44}N_4O_2$: C, 71.76; H, 9.46; N, 11.95. Found: C, 71.86; H, 9.51; N, 11.76.

Tetra(*N*-benzyl) DBTA-18-Crown-6 (10c). Colorless, glass-like solid (65%); mp <40 °C; ^{1}H NMR ($CDCl_3$) δ 3.36 (br s, 16H), 4.35 (s, 8H), 6.83 (s, 8H), 7.10−7.19 (m, 20H); ^{13}C NMR ($CDCl_3$) δ 48.8, 56.2, 67.3, 121.4, 122.0, 126.8, 128.1, 128.9, 138.6, 143.5; MS (relative intensity) *m/z* 717 ($M^+ + 1$, 100%), 625 ($M^+ - Bz$), 534 ($M^+ - 2Bz$); HRMS calcd for $C_{48}H_{53}N_4O_2$ 717.4169, found 717.4161.

Tetra(*N*-ethyl) DBTA-24-Crown-8 (10d). Colorless, crystalline solid (21%); mp 32−33 °C; ^{1}H NMR (CDCl$_3$) δ 0.97 (t, 12H, J = 6.79 Hz), 3.22 (q, 8H, J = 7.12 Hz), 3.36 (t, 8H, J = 6.20 Hz), 3.45 (s, 8H), 3.5 (t, 8H, J = 6.21 Hz), 6.9 (s, 8H); ^{13}C NMR (CDCl$_3$) δ 12.0, 45.4, 49.8, 68.9, 70.1, 121.2, 121.6, 144.0; MS (relative intensity) *m/z* 556 (M$^+$, 16.5%), 278 (M$^+$/2), 175 (100%); HRMS calcd for $C_{32}H_{53}N_4O_4$ 557.4067, found 557.4096. Anal. Calcd for $C_{32}H_{52}N_4O_4$: C, 69.03; H, 9.41; N, 10.06. Found: C, 68.93; H, 9.18; N, 9.89.

Tetra(*N*-methyl)tetrabenzotetraaza-24-Crown-8 (10e). Colorless, viscous oil (31%); ^{1}H NMR (CDCl$_3$) δ 2.83 (s, 12H), 3.57 (t, 8H, J = 5.90 Hz), 4.05 (t, 8H, J = 5.62 Hz), 6.74 (s, 8H), 6.96 (s, 8H); ^{13}C NMR (CDCl$_3$) δ 40.1, 53.0, 67.3, 114.6, 119.6, 121.2, 122.3, 145.5, 149.2; MS (relative intensity) *m/z* 597 (M$^+$ + 1, 100%); HRMS calcd for $C_{36}H_{45}N_4O_4$ 597.3441, found 597.3441.

Tetramethyl DBTA-18-crown-6 Diformamide (13). The ether was obtained as a mixture of two isomers. The preparation followed the one described for tetramethyl DBTA-18-crown-6 (**2h**), except that the reaction was carried out at 110 °C in an ethanol−*n*-propanol 4:1 mixture. Potassium hydroxide (1.00 g) and ditosylate ($\cdot$CH$_3$NO$_2$) **8h** (0.50 g, 0.60 mmol) in 15 mL of the 4:1 solvent were heated for 2 h. A colorless precipitate formed. The solution was cooled to room temperature, followed by the addition of water (50 mL). This caused the formation of more precipitate. The combined solids were collected by filtration and thoroughly rinsed with water (until pH = 7). The product was not purified further. Colorless powder (58%); mp 196−202 °C; ^{1}H NMR (CDCl$_3$) δ 2.14 (s, 6H), 2.23 (s, 6H), 3.25 (br s, 8H), 3.5−3.7 (br s, 8H), 5.39 (br s, 2H), 6.48 (s, 2H), 6.74 (s, 2H), 8.09 (s, 2H, −CHO); MS (relative intensity) *m/z* 468 (M$^+$, 34.8%), 449 (100%); HRMS calcd for $C_{26}H_{36}N_4O_4$ 468.2737, found 468.2739. Anal. Calcd for $C_{26}H_{36}N_4O_4$: C, 66.64; H, 7.74; N, 11.96. Found: C, 66.39; H, 7.95; N, 11.72.

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Supporting Information Available: Crystallographic data in CIF format; general experimental information; experimental procedures and analytical data for bis(benzimidazolyl)ethers **6a**−**o**, 2-(1′-benzimidazolyl)ethyl vinyl sulfide **12**, and 2,3-bis(2′-chloroethoxy)naphthalene **16**; ^{1}H and ^{13}C NMR spectra of **10c**, **10e**, and **12**; ^{1}H NMR spectrum of **14**; X-ray crystal structure for **8o**; X-ray crystallographic data for **8o** and **9c**; and experimental procedures for picrate extraction studies. This material is available free of charge via the Internet at http://pubs.acs.org.

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