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Synthesis of New Lipophilic Acyclic Di-ionizable Polyethers, Bis(Crown Ethers) and Macrocyclic Diamides

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Abstract: A series of new lipophilic acyclic polyethers containing two carboxylic or hydroxamic acid groups have been prepared. From lipophilic acyclic polyether dicarboxylic acids **2**, **9** and **13**, the bis(crown ethers) **20-25** were synthesized. From lipophilic acyclic polyether dicarboxylic acids **10-12** and **14**, the new macrocyclic diamides **26-32** were prepared in high yields without the use of high dilution techniques or template effects. © 1999 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Strong complexation of alkali metal cations by acyclic, naturally occurring antibiotics, such as nigericin and monensin, has prompted the systematic study of synthetic acyclic polyethers, which have certain advantages over their cyclic analogues. Complex stability and ion selectivity can often be achieved with the synthetically more accessible acyclic polyethers.[1] Complexation and decomplexation processes are generally faster in the acyclic systems and the pseudocavity usually has greater conformational flexibility.[1]

Marchelli and coworkers[2] reported the synthesis and complexing properties of acyclic ligands containing L-phenylalanine units and found that these compounds were effective and selective ligands for the extraction of UO_2^{2+} and alkaline earth cations.[3] Hiratani and coworkers[4,5] prepared a series of acyclic polyethers with two *o*-carboxyphenyl terminal units, as well as related compounds with 3-carboxy-2-hydroxyphenyl end groups. These compounds exhibited fairly good Ca^{2+} selectivity in solvent extraction and Ba^{2+} selectivity in transport across synthetic membranes. Bartsch and coworkers[6,7] evaluated three series of lipophilic acyclic polyether dicarboxylic acids and one series of lipophilic acyclic polyether phosphonic acid monoethyl esters in the competitive extraction of alkaline earth cations from aqueous solutions into chloroform. The efficiency and selectivity with which the former extracted alkaline earth cations was strongly influenced by the structure of the ligand. More recently, Hayashita *et al.*[8] reported that certain dibenzo polyether dicarboxylic acid ionophores exhibit high extraction selectivity for Pb^{2+} over Cu^{2+}.

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The observation that some crown ethers form complexes involving two ligands per metal ion led several research groups to prepare and examine the metal ion-complexation properties of bis(crown ethers).[9-15] Such ligands may form intramolecular sandwich complexes in which the proximate crown ether units cooperate.[10-14] Due to such interactions, certain bis(crown ethers) exhibit remarkable selectivity toward specific metal ions when incorporated into solvent polymeric membrane electrodes.[11] Bis(crown ether) diesters with a short aliphatic chain linking two crown ether ester groups complex certain metal cations strongly and selectively by formation of intramolecular sandwich complexes.[9-12] Zavada and coworkers prepared a series of bis(monoazacrown ethers) and studied the effects of linker length and ring size on the strength and selectivity of alkali metal cation complexation.[13] They observed that both the size of the azacrown ether ring and the length of the linker strongly influenced the selectivity of alkali metal cation complexation.[13a] Recently, we reported the preparation of a series of bis(crown ethers) in which the linker between two *sym*-dibenzo-16-crown-5 units contained a carboxylic acid unit, an amide group, two amide functions or two ester groups.[16] For a recently reported series of bis(crown ethers) derived from xanthene-4,5-dicarboxylic acid, those containing 15-crown-5 and 18-crown-6 rings exhibited pronounced extraction selectivities for K^+ and Cs^+, respectively.[17]

Incorporation of an amide linkage in a polyether macrocycle may modify the binding properties of crown ether compounds to favor alkaline earth cations with respect to alkali metal cations.[18-23] Gokel and coworkers have found that diaza-18-crown-6 derivatives with amide groups in their side arms exhibit extraordinary Ca^{2+} binding strength and remarkable selectivity for Ca^{2+} over Na^+,[24] while a number of synthetic cyclopeptides are K^+ or Ca^{2+} ionophores.[25] Also macrocyclic diamides are precursors in the preparation of diazacrown compounds which are used as molecular receptors and for the synthesis of cryptands and related compounds.[26,27]

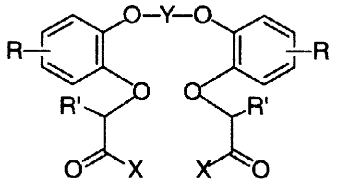
We now report the preparation of a series of lipophilic acyclic polyether dicarboxylic acids **1-17** (Figure 1) and the use of certain members of the series as starting materials for the synthesis of lipophilic acyclic polyether dihydroxamic acids **18** and **19** (Figure 1), new lipophilic bis(crown ethers) **20-25** (Figure 2), and lipophilic macrocyclic crown ether diamides **26-32** (Figure 3).

RESULTS AND DISCUSSION

Synthesis of Lipophilic Acyclic Polyether Dicarboxylic Acids

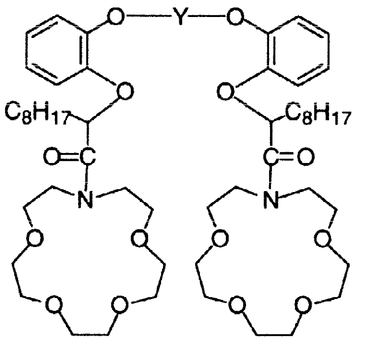
New acyclic polyether dicarboxylic acids **1-17** were prepared by reaction of the appropriate bisphenol and 2-bromocarboxylic acids with NaH in THF in 60-90% yields as shown in Scheme 1. Although **2**, **5**, **7** and **11** are known compounds, the current synthetic route is more efficient than the reported methods.

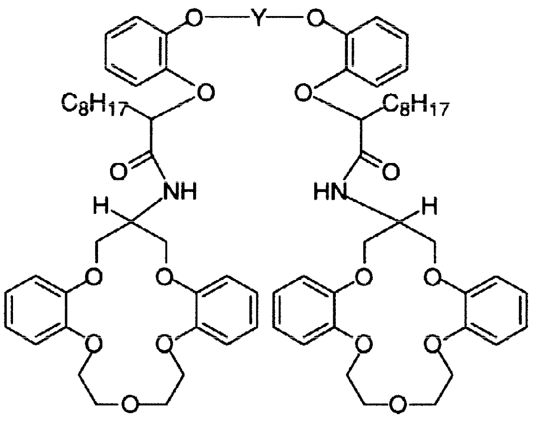
For probing the influence of ligand structure upon the efficiency and selectivity of multivalent metal ion complexation, this group of acyclic polyether dicarboxylic acids contains several series with systematic structural variations. For compounds **1-7**, the spacer Y is an ethylene unit and the identity of the lipophilic R' group is systematically varied from heptyl to octyl to nonyl to decyl to dodecyl to tetradecyl to hexadecyl. Analogue **8** has the same spacer and R' = phenyl. In acyclic polyether dicarboxylic acids **9** and **10**, the spacer is elongated to a 1,3-propylene unit and the R' groups are octyl and tetradecyl, respectively. For the series of compounds **11** and



	Y	R	R'	X
1	CH_2CH_2	H	C_7H_{15}	OH
2	CH_2CH_2	H	C_8H_{17}	OH
3	CH_2CH_2	H	C_9H_{19}	OH
4	CH_2CH_2	H	$C_{10}H_{21}$	OH
5	CH_2CH_2	H	$C_{12}H_{25}$	OH
6	CH_2CH_2	H	$C_{14}H_{29}$	OH
7	CH_2CH_2	H	$C_{16}H_{33}$	OH
8	CH_2CH_2	H	C_6H_5	OH
9	$CH_2CH_2CH_2$	H	C_8H_{17}	OH
10	$CH_2CH_2CH_2$	H	$C_{14}H_{29}$	OH
11	$CH_2CH_2OCH_2CH_2$	H	H	OH
12	$CH_2CH_2OCH_2CH_2$	*t*-Bu	H	OH
13	$CH_2CH_2OCH_2CH_2$	H	C_8H_{17}	OH
14	$CH_2CH_2OCH_2CH_2$	H	$C_{14}H_{29}$	OH
15	$CH_2CH_2OCH_2CH_2$	H	C_6H_5	OH
16	$CH_2(CH_2OCH_2)_2CH_2$	H	$C_{14}H_{29}$	OH
17	$CH_2C(O)NH(CH_2)_2NHC(O)CH_2$	H	$C_{14}H_{29}$	OH
18	$CH_2CH_2OCH_2CH_2$	*t*-Bu	H	NHOH
19	$CH_2CH_2OCH_2CH_2$	H	$C_{14}H_{29}$	NHOH

Figure 1

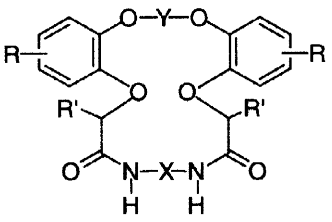




	Y	
20	CH_2CH_2	**23**
21	$CH_2CH_2CH_2$	**24**
22	$CH_2CH_2OCH_2CH_2$	**25**

Figure 2

13-**15**, the spacer is -$CH_2CH_2OCH_2CH_2$- and R' is hydrogen, octyl, tetradecyl and phenyl. Compared with **11**, compound **12** is identical except for the introduction of a lipophilic *tert*-butyl group on each benzene ring of the



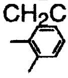
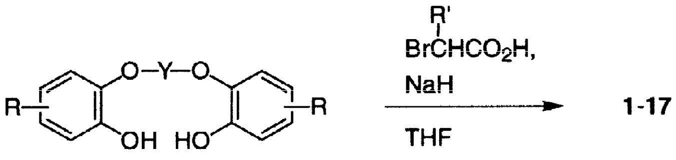
	Y	R	R'	X
26	$CH_2CH_2CH_2$	H	$C_{14}H_{29}$	CH_2CH_2
27	$CH_2CH_2CH_2$	H	$C_{14}H_{29}$	$CH_2CH_2CH_2$
28	$CH_2CH_2OCH_2CH_2$	H	H	CH_2CH_2
29	$CH_2CH_2OCH_2CH_2$	*t*-Bu	H	CH_2CH_2
30	$CH_2CH_2OCH_2CH_2$	H	$C_{14}H_{29}$	CH_2CH_2
31	$CH_2CH_2OCH_2CH_2$	H	$C_{14}H_{29}$	$CH_2CH_2CH_2$
32	$CH_2CH_2OCH_2CH_2$	H	$C_{14}H_{29}$	

Figure 3



	Y	R
33	CH_2CH_2	H
34	$CH_2CH_2CH_2$	H
35	$CH_2CH_2OCH_2CH_2$	H
36	$CH_2CH_2OCH_2CH_2$	*t*-Bu
37	$CH_2(CH_2OCH_2)_2CH_2$	H
38	$CH_2C(O)NH(CH_2)_2NHC(O)CH_2$	H

Scheme 1

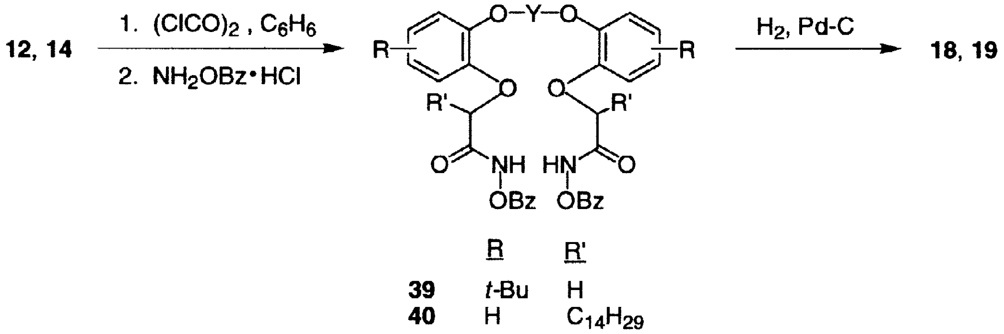
ligand. For the series of compounds **2**, **9** and **13** and of **6**, **10**, **14** and **16** the lipophilic group is held constant and the spacer group is systematically varied from ethylene to 1,3-propylene to $-CH_2CH_2OCH_2CH_2-$ and in the latter seris to $-CH_2(CH_2OCH_2)_2CH_2-$. The diether spacer in **16** is replaced with an analogous diamide spacer in **17**, while holding the lipophilic group constant.

Lipophilic acyclic polyether dicarboxylic acids **14** and **16** have been used for the separation of $^{90}Y^{3+}$ from $^{90}Sr^{2+}$ by solvent extraction[28].

Synthesis of Lipophilic Acyclic Polyether Dihydroxamic Acids

The lipophilic acyclic polyether dicarboxylic acids **12** and **14** were transformed into analogous hydroxamic acids **18** and **19** in 81-90% yields as shown in Scheme 2.

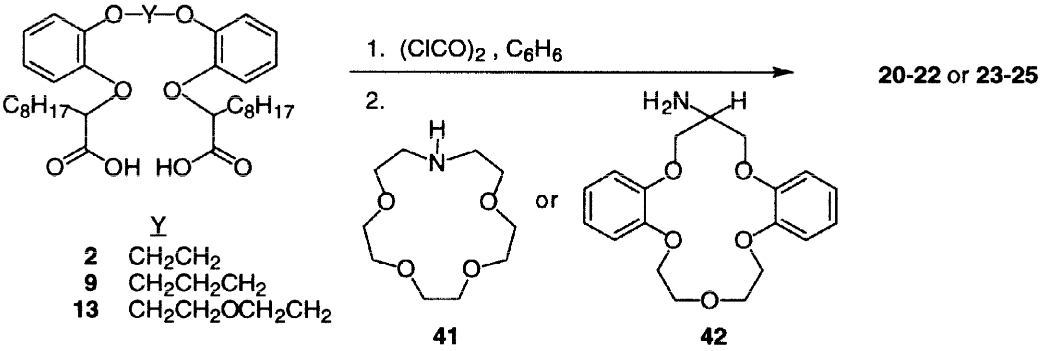
In competitive solvent extraction of trivalent lanthanides, lipophilic acyclic polyether dihydroxamic acids exhibited greater efficiency and selectivity than the corresponding dicarboxylic acids.[29]



Scheme 2

Synthesis of Lipophilic Bis(Crown Ethers)

Lipophilic acyclic polyether dicarboxylic acids **2**, **9** and **13** were employed in the synthesis of the new bis(crown ether) compound series **20-25** (Scheme 3). By reaction with oxalyl chloride, the dicarboxylic acid was converted into the corresponding diacid chloride. Treatment of the diacid chloride with monoaza-15-crown-5 or *sym*-(amino)dibenzo-16-crown-5 in the presence of Et_3N in CH_2Cl_2 gave the bis(crown ethers) in 41-90% yields. Bis(crown ethers) **20-25** are sufficiently lipophilic to remain in an organic medium when contacted with an aqueous solution. For the series of new bis(crown ethers) **20-22** and **23-25**, the spacer which joins the two crown ether units is systematically varied from ethylene to 1,3-propylene to $-CH_2CH_2OCH_2CH_2-$. This adjusts the distance between the two crown ether rings which may have an important influence upon the efficiency and selectivity of metal ion-sandwich complex formation.[9,13]

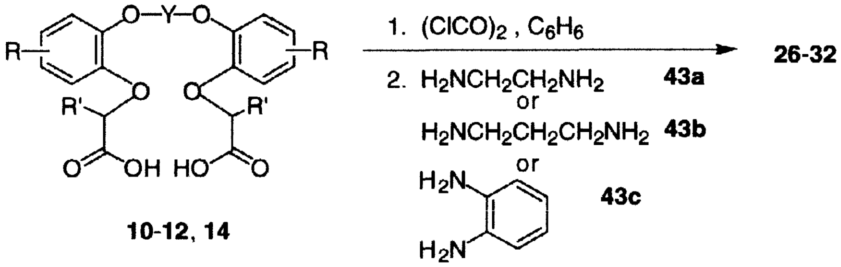


Scheme 3

Synthesis of Lipophilic Macrocyclic Diamides

Lipophilic acyclic polyether dicarboxylic acids **10-12** and **14** were used for the preparation of lipophilic macrocyclic diamides.

For the formation of diaza macrocyclic compounds, several synthetic methods have been developed. Among these methods, the high dilution technique is often used as the most versatile procedure.[26] However, this technique is inconvenient since it requires the simultaneous addition of a diamine and diacid chloride to a large volume of solvent over an extended period of time. Recently Sharghi and coworkers reported the preparation of several macrocyclic diamides by reacting the diacid chloride with diamines in CH_2Cl_2 without the use of high dilution.[30] This finding led us to apply a similar approach for the synthesis of lipophilic macrocyclic polyether diamides (Scheme 4).



Scheme 4

The lipophilic acyclic polyether dicarboxylic acids **10-12** and **14** were converted into diacid chlorides with oxalyl chloride. Cyclization was accomplished by rapid addition of a mixture of the diamine and triethylamine in CH_2Cl_2 to a stirred solution of the diacid chloride in CH_2Cl_2 at 0 °C followed by further stirring at room temperature for 15 minutes and workup to give lipophilic macrocyclic diamides **26-32** in 80-96% yields.

Structures of the new lipophilic acyclic polyether dicarboxylic and hydroxamic acids, bis(crown ethers) and macrocyclic diamides were consistent with their IR and NMR spectra and verified by elemental analysis.

Further investigation of the extraction efficiency and selectivity of these acyclic di-ionizable polyethers, bis(crown ethers) and macrocyclic diamides are in progress in our laboratories and the results will be reported in due course.

EXPERIMENTAL

Materials and Methods. The ^1H NMR spectra were recorded with a Bruker AF 200 spectrometer (200 MHz) in $CDCl_3$ with tetramethylsilane as the internal standard. IR spectra were measured with a Digilab Qualimatic FTS-80 spectrophotometer. Mass spectra were obtained on a VG Micro mass 70/70 HS mass spectrometer. Melting points were measured with a Thomas-Hoover melting point apparatus and are uncorrected. Tetrahydrofuran (THF) was distilled from sodium and benzophenone. Starting materials **33**,[31] **34**,[32] **35**,[33] **36**,[34] **37**[32], **38**[35] and **41**[36] were prepared as reported. Elemental analysis was performed by Desert Analytics Laboratory, Tucson, AZ.

General Procedure for the Preparation of Acyclic Polyether Dicarboxylic Acids 1-17. A mixture of 1.20 g (50 mmol) of NaH and 30 mL of THF was stirred under nitrogen for 30 min at room temperature and then a solution of 5.0 mmol of the appropriate bisphenol in 50 mL of THF was added dropwise during 1 h. The mixture was stirred for 1 h at room temperature and then a solution of 15-20 mmol of the α-bromocarboxylic acid in 50 mL of THF was added during 1-2 h. The reaction mixture was stirred for 24 h at room temperature (refluxed overnight for **11** and **12**). Water was carefully added to destroy the excess of NaH and the THF was evaporated in vacuo. Water was added to the residue and the mixture was acidified with 6 N HCl and extracted with CH_2Cl_2. The CH_2Cl_2 layer was washed with water, dried over $MgSO_4$ and evaporated in vacuo to give the crude product which was purified by recrystallization or column chromatography.

1,2-Di[2-(2'-carboxynonyloxy)phenoxy]ethane (**1**) with mp 128-130 °C was obtained in 90% yield after recrystallization from hexanes: IR (KBr) 3435 (COOH), 1702 (C=O) cm^{-1}; ^1H NMR δ 0.88 (t, 6H, J = 6 Hz), 1.25 (s, 16H), 1.53-1.60 (m, 4H), 1.95-2.02 (m, 4H), 4.40 (s, 4H), 4.52-4.56 (m, 2H), 6.96-7.07 (m, 8H). Anal. Calcd for $C_{32}H_{46}O_8$: C, 68.79; H, 8.30. Found: C, 68.58; H, 8.43.

1,2-Di[2-(2'-carboxydecyloxy)phenoxy]ethane (**2**) with mp 119-121 °C was prepared in 96% yield after recrystallization from hexanes: IR (KBr) 3436 (COOH), 1708 (C=O) cm^{-1}; ^1H NMR δ 0.87 (t, 6H, J = 6 Hz), 1.25 (s, 20H), 1.53 (m, 4H), 1.90-1.97 (m, 4H), 4.40 (s, 4H), 4.53-4.57 (m, 2H), 6.94-7.01 (m, 8H). Anal. Calcd for $C_{34}H_{50}O_8$: C, 69.60; H, 8,59. Found: C, 69.51; H, 8.21.

1,2-Di[2-(2'-carboxyundecyloxy)phenoxy]ethane (**3**) with mp 119-121 °C was realized in 86% yield after recrystallization from hexanes: IR (KBr) 3439 (COOH), 1703 (C=O) cm^{-1}; ^1H NMR δ 0.87 (t, 6H, J = 6 Hz), 1.23 (s, 24H), 1.47-1.52 (m, 4H), 1.91-1.98 (m, 4H), 4.38 (s, 4H), 4.51-4.57 (m, 2H), 6.90-7.07 (m, 8H), 9.80 (br s, 2H). Anal. Calcd for $C_{36}H_{54}O_8 \cdot 0.5H_2O$: C, 69.36; H, 8.89. Found: C, 69.37; H, 9.11.

1,2-Di[2-(2'carboxydodecyloxy)phenoxy]ethane (**4**) with mp 108-110 °C was obtained in 97% yield after recrystallization from hexanes: IR (KBr) 3429 (COOH), 1706 (C=O) cm^{-1}; ^1H NMR δ 0.87 (t, 6H, J = 6 Hz), 1.23 (s, 28H), 1.52 (m, 4H), 1.93-2.01 (m, 4H), 4.39 (s, 4H), 4.51-4.54 (m, 2H), 6.94-7.05 (m, 8H). Anal. Calcd for $C_{38}H_{58}O_8$: C, 71.00; H, 9.09. Found: C, 71.02; H, 9.31.

1,2-Di[2-(2'-carboxytetradecyloxy)phenoxy]ethane (**5**) with mp 100-101 °C was isolated in 93% yield after recrystallization from hexanes: IR (KBr) 3425 (COOH), 1708 (C=O) cm^{-1}; ^1H NMR δ 0.88 (t, 6H, J = 6 Hz), 1.24 (s, 36H), 1.53-1.55 (m, 4H), 1.92-1.99 (m, 4H), 4.38 (s, 4H), 4.49-4.56 (m, 2H), 6.92-7.09 (m, 8H). Anal. Calcd for $C_{42}H_{66}O_8$: C, 72.17; H, 9.52. Found: C, 72.23; H, 9.79.

1,2-Di[2-(2'-carboxyhexadecyloxy)phenoxy]ethane (**6**) with mp 101-102 °C was produced in 98% yield after recrystallization from hexanes: IR (KBr): 3432 (COOH), 1701 (C=O) cm^{-1}; ^1H NMR δ 0.88 (t, 6H, J = 6 Hz), 1.25 s, 44H), 1.53-1.55 (m, 4H), 1.92-1.99 (m, 4H), 4.40 (s, 4H), 4.49-4.56 (m, 2H), 6.92-7.10 (m, 8H). Anal. Calcd for $C_{46}H_{74}O_8$: C, 73.17; H, 9.88. Found: C, 72.99; H, 10.01.

1,2-Di[2-(2'carboxyoctadecyloxy)phenoxy]ethane (**7**) with mp 107-109 °C was obtained in 98% yield after recrystallization from hexanes: IR (KBr) 3448 (COOH), 1708 (C=O) cm^{-1}; ^{1}H NMR δ 0.88 (t, 6H, *J* = 6 Hz), 1.25 (s, 52H), 1.53 (m, 4H), 1.92-1.99 (m, 4H), 4.40 (s, 4H), 4.51-4.57 (m, 2H), 6.91-7.08 (m, 8H). Anal. Calcd for $C_{50}H_{82}O_8$; C, 74.03; H, 10.19. Found: C, 73.94; H, 10.11.

1,2-Di[(α-carboxybenzyloxy)phenoxy]ethane (**8**) with mp 144-146 °C was realized in 86% yield after recrystallization from EtOAc-hexanes: IR (KBr) 3450 (COOH), 1718 (C=O) cm^{-1}; ^{1}H NMR δ 4.08-4.15 (m, 4H), 5.51 (s, 2H), 6.83-7.04 (m, 8H), 7.24-7.47 (m, 6H), 7.48-7.50 (m, 4H), 9.21 (br s, 2H). Anal. Calcd for $C_{30}H_{26}O_8$: C, 70.04; H, 5.09. Found: C, 70.41; H, 5.26.

1,2-Di[2-(2'-carboxydecyloxy)phenoxy]propane (**9**) with mp 123-125 °C was isolated in 81% yield after recrystallization from hexanes: IR (KBr) 3451 (COOH), 1702 (C=O) cm^{-1}; ^{1}H NMR δ 0.87 (t, 6H, *J* = 6Hz), 1.26 (s, 20H), 1.55-1.58 (m, 4H), 1.91-2.01 (m, 4H), 2.28-2.38 (m, 2H), 4.15-4.28 (m, 4H), 4.37-4.47 (m, 2H), 6.65-7.09 (m, 8H). Anal. Calcd for $C_{35}H_{52}O_8$: C, 69.97; H, 8.72. Found: C, 70.22; 8.79.

1,2-Di[2-(2'-carboxyhexadecyloxy)phenoxy]propane (**10**) with mp 92-94 °C was obtained in 74% yield after recrystallization from EtOH: IR (KBr) 3452 (COOH), 1706 (C=O) cm^{-1}; ^{1}H NMR δ 0.85 (t, 6H, *J* = 6Hz), 1.23 (s, 44H), 1.53 (q, 4H, *J* = 6 Hz), 1.89-2.00 (m, 4H), 4.17 (t, 4H, *J* = 6 Hz), 4.42 (t, 4H, *J* = 6 Hz), 6.84-7.02 (m, 8H). Anal. Calcd for $C_{47}H_{76}O_8 \bullet 0.75\ H_2O$: C, 72.13; H, 9.98. Found: C, 71.92; H, 9.97.

1,5-Di(2'-acetoxyphenoxy)-3-oxapentane (**11**) with mp 141-142 °C (lit.[37] 143 °C) was obtained as a white solid in 60% yield after drying with toluene in a Dean-Stark apparatus: IR (KBr) 3471 (COOH), 1724 (C=O) cm^{-1}; ^{1}H NMR δ 3.91-3.94 (m, 4H), 4.18-4.21 (m, 4H), 4.70 (s, 4H), 6.84-7.03 (m, 8H). In the literature **11** was obtained by a different method.[37]

1,5-Di[2-acetoxy-4(5)-tert-butylphenoxy]-3-oxapentane (**12**) was obtained in 80% yield as a colorless oil which solidified on standing; IR (deposit from CH_2Cl_2 on a NaCl plate) 3491 (COOH), 1743 (C=O) cm^{-1}; ^{1}H NMR δ 1.43 (s, 18H), 4.10-4.81 (m, 12H), 6.95-7.18 (m, 6H), 7.58 (br s, 2H). Anal. Calcd for $C_{28}H_{38}O_9$: C, 64.84; H, 7.39. Found: C, 64.68; H, 7.67.

1,5-Di[2-(2'-carboxydecyloxy)phenoxy]-3-oxapentane (**13**) with mp 108-110 °C was produced in 90% yield after recrystallization from hexanes: IR (KBr) 3432 (COOH), 1701 (C=O) cm^{-1}; ^{1}H NMR δ 0.87 (t, 6H, *J* = 6 Hz), 1.25 (s, 20H), 1.55 (m, 4H), 1.89-1.97 (m, 4H), 3.68-3.93 (m, 4H), 4.15-4.19 (m, 4H), 4.49-4.53 (m, 2H), 6.90-7.03 (m, 8H), 8.90 (br s, 2H). Anal. Calcd for $C_{36}H_{54}O_9$: C, 68.54; H, 8.63. Found: C, 68.58; H, 8.79.

1,5-Di[2-(2'-carboxyhexadecyloxy)phenoxy]-3-oxapentane (**14**) with mp 77-79 °C was prepared in 83% yield after recrystallization from *n*-hexane: IR (KBr) 3433 (COOH), 1705 (C=O) cm^{-1}; ^{1}H NMR δ 0.87 (t, 6H, *J* = 6 Hz), 1.23 (s, 44H), 1.42 (q, 4H, *J* = 6 Hz), 1.83-1.84 (m, 4H), 3.90 (s, 4H), 4.15 (s, 4H), 4.47 (m, 2H), 6.92-7.01 (m, 8H). Anal. Calcd for $C_{48}H_{78}O_9$: C, 72.14; H, 9.83. Found: C, 71.86; H, 9.68.

1.5-Di[(α-carboxybenzyloxy)phenoxy]-3-oxapentane (**15**) with mp 41-43 °C was obtained in 70% yield after chromatography on silica gel with CH_2Cl_2:MeOH (9:1) as eluent as an oil which solidified after drying in vacuo: IR (KBr) 3417 (COOH), 1732 (C=O) cm^{-1}; ^{1}H NMR δ 3.94-3.98 (m, 4H); 4.16-4.24 (m, 4H), 5.47 (s, 2H), 6.78-7.02 (m, 8H), 7.31-7.33 (m, 6H), 7.49-7.52 (m, 4H). 8.60 (br s, 2H). Anal. Calcd for $C_{32}H_{30}O_9$: C, 68.80; H, 5.41. Found: C, 68.48; H, 5.56.

1,8-Di[2-(2'-carboxyhexadecyloxy)phenoxy]-3-oxapentane (**16**) with mp 67-69 °C) was realized in 83% yield after recrystallization from *n*-pentane-*n*-hexane: IR (KBr) 3437 (COOH), 1705 (C=O) cm^{-1}; ^{1}H NMR δ 0.85 (t, 6H, *J* = 6Hz), 1.23 (s, 44H), 1.41 (q, 4H, *J* = 6Hz), 1.73-1.96 (m, 4H), 3.77-4.86 (m, 4H), 6.84-6.99 (m, 8H). Anal. Calcd for $C_{50}H_{82}O_{10}$: C, 71.22; H, 9.80. Found: C, 71.36; H, 9.68.

Lipophilic diamide dicarboxylic acid **17** with mp 114-116 °C was obtained in 62% yield after recrystallization from *n*-pentane: IR (KBr): 3448, 3379 (COOH), 3317 (NH), 1732 (C=O, carboxy), 1635 (C=O, amido) cm^{-1}; ^{1}H NMR δ 0.84 (t, 6H, *J* = 6 Hz), 1.22 (s, 44H), 1.48 (q, 4H, *J* = 6 Hz), 1.87-2.08 (m, 4H), 3.20-3.27 (m, 4H), 3.87 (s, 2H), 4.46-4.62 (m, 4H), 6.25 (s, 2H), 6.78-6.98 (m, 8H), 8.00 (s, 2H, NH). Anal. Calcd for $C_{50}H_{80}N_2O_{10}$•H_2O: C, 67.72; H, 9.14; N, 3.16. Found: C, 67.47; H, 9.08; N, 3.00.

General Procedure for the Preparation of Acyclic Polyether Dihydroxamic Acids 18 and 19 via O-Benzyl Hydroxamates 39 and 40. To a solution of the acyclic polyether dicarboxylic acids **12** or **14** (1.50 mmol) in 10 mL of dry benzene at 0 °C under nitrogen, oxalyl chloride (12 mmol) was added dropwise. The reaction mixture was stirred for 1 h at room temperature then for 1 h at 60-70 °C and evaporated in vacuo. The diacid chloride product was used immediately in the next step.

To O-benzylhydroxylamine hydrochloride (0.48 g, 3.0 mmol) suspended in 10 mL of dry MeCN, pyridine (6 mmol) was added. The mixture was cooled to 0 °C and an MeCN solution of the diacid chloride was added dropwise. The mixture was allowed to warm to room temperature, stirred for 24 h and evaporated in vacuo. The residue was dissolved in EtOAc. The solution was washed twice with 0.6 N HCl, once with water, once with aq $NaHCO_3$, and again with water. The mixture was dried over $MgSO_4$ and evaporated in vacuo to give the lipophilic acyclic polyether di(O-benzyl hydroxamate).

1,5-Di[O-benzyl 2-oxymethylenehydroxamato-4(5)-tert-butylphenoxy]-3-oxapentane (**39**) was obtained in 90% yield as an oil which was of suitable purity for use in the next step: IR (deposit from $CHCl_3$ on a NaCl plate) 3271 (NH), 1689 (C=O) cm^{-1}; ^1H NMR δ 1.23 (s, 18H), 3.69-4.14 (m, 8H), 4.55 (s, 4H), 4.85 (s, 4H), 6.72, 7.32 (m, 16H), 9.94 (br s, 2H).

1,5-Di[2-(2'-O-benzyl hydroxamatohexadecyloxy)phenoxy]-3-oxapentane (**40**) with mp 95-97 °C was obtained in 81% yield after recrystallization from EtOAc: IR (KBr): 3182 (NH), 1666 (C=O) cm^{-1}; ^1H NMR δ 0.84 (t, 6H, $J = 6$ Hz), 1.22 (s, 44H), 1.45 (q, 4H, $J = 6$ Hz), 1.84-1.92 (m, 4H), 3.72-3.96 (m, 6H), 4.42-4.58 (m, 4H), 4.79 (s, 4H), 6.96-7.73 (m, 8H), 7.23-7.35 (m, 10H), 9.95 (br s, 2H, NH).

The O-benzylhydroxamate (1.0 mmol) was dissolved in 150 mL of MeOH and stirred under hydrogen at room temperature and atmospheric pressure with 10% Pd/C (200 mg) as catalyst. After 30 min, the catalyst was filtered and the MeOH evaporated in vacuo. Hydroxamic acids **18** and **19** gave positive tests with Fe^{3+}.

1,5-Di[2-oxymethylenehydroxamato-4(5)-tert-butylphenoxy]-3-oxapentane (**18**) was obtained in 95% yield as an oil which solidified on standing; IR (KBr) 3244 (NHOH), 1674 (C=O) cm^{-1}; ^1H NMR δ 1.23 (s, 18H), 3.97-4.19 (m, 8H), 4.59 (s, 4H), 6.70-6.94 (m, 6H), 11.02 (s, 2H, NH). Anal. Calcd for $C_{28}H_{40}N_2O_9{\bullet}H_2O$: C, 59.35; H, 7.47; N, 4.94. Found: C, 59.21; H, 7.44; N, 4.78.

1,5-Di[2-(2'-hydroxamatohexadecyloxy)phenoxy]-3-oxapentane (**19**) with mp 110-112 °C was obtained in 80% yield after recrystallization from MeOH: IR (KBr): 3402, 3166 (NHOH), 1639 (C=O) cm^{-1}; ^1H NMR δ 0.84 (t, 6H, $J = 6$ Hz), 1.22 (s, 44H), 1.44 (q, 4H, $J = 6$ Hz), 1.86-1.93 (m, 4H), 3.75-4.62 (m, 10H), 6.72-6.95 (m, 8H), 11.00 (s, 2H, NH). Anal. Calcd for $C_{48}H_{80}N_2O_9$: C, 69.53; H, 9.72; N, 3.37. Found: C, 69.47; H, 9.65; N, 3.66.

General Procedure for the Preparation of Bis(Crown Ethers) 20-25. The diacid chlorides of dicarboxylic acids **2**, **9** and **13** were prepared as in the previous section. The crude diacid chloride was dissolved in CH_2Cl_2 and the solution was added dropwise to a stirred solution of 2 equiv of monoaza-15-crown-5 or *sym*-(amino)dibenzo-16-crown-5 and Et_3N (2 equiv) in CH_2Cl_2. The reaction mixture was stirred for 24 h at room temperature, washed with 1 N HCl and water, dried over Na_2SO_4 and evaporated in vacuo. The crude product was purified by chromatography on silica gel with CH_2Cl_2 then CH_2Cl_2-EtOAc (4:1) as eluents for compounds **20-22** or with CH_2Cl_2-MeOH (19:1) as eluents for compounds **23-25**.

Bis(crown ether) ***20*** was obtained in 77% yield as an oil: IR (film) 1654 (C=O) cm^{-1}; ^1H NMR δ 0.86 (t, 6H, *J* = 6 Hz), 1.25 (s, 24H), 1.99 (m, 4H), 3.48-3.67 (m, 40H), 4.39 (s, 4H), 4.89 (m, 2H), 6.88-7.00 (m, 8H). Anal. Calcd for $C_{54}H_{88}N_2O_{14}$: C, 65.55; H, 8.96; N, 2.84. Found: C, 65.28; H, 8.91; N, 2.80.

Bis(crown ether) ***21*** was realized in 90% yield as an oil: IR (film) 1654 cm^{-1}; ^1H NMR δ 0.86 (t, 6H, *J* = 6 Hz), 1.25 (s, 24H), 1.84-2.00 (m, 4H), 2.28-2.33 (m, 2H), 3.54-3.59 (m, 40H), 4.19-4.26 (m, 4H), 4.80-4.87 (m, 2H), 6.80-6.93 (m, 8H). Anal. Calcd for $C_{55}H_{90}N_2O_{14}$: C, 65.83; 9.04; N, 2.80. Found: C, 65.62; H, 9.00; N, 2.63.

Bis(crown ether) ***22*** was isolated in 78% yield as an oil: IR (film): 1657 (C=O) cm^{-1}; ^1H NMR δ 0.86 (t, 6H, *J* = 6Hz), 1.25 (s, 24H), 1.60-1.99 (m, 4H), 3.45-3.67 (m, 40H), 3.90-3.95 (m, 4H), 4.17-4.22 (m, 4H), 4.85-4.92 (m, 2H), 6.80-7.08 (m, 8H). Anal. Calcd for $C_{56}H_{92}N_2O_{15}$: C, 65.08; H, 8.97; N, 2.72. Found: C, 65.05; H, 9.09; N, 2.59.

Bis(crown ether) ***23*** with mp 158-160 °C was obtained in 51% yield: IR (deposit from CH_2Cl_2 solution on a NaCl plate) 3368, 3276 (NH), 1732 (C=O) cm^{-1}; ^1H NMR δ 0.84 (t, 6H, *J* = 6 Hz), 1.18 (s, 20H), 1.48 (m, 4H), 1.89-1.91 (m, 4H), 3.74-3.96 (m, 8H), 3.98-4.36 (m, 16H), 4.43-4.63 (m, 8H), 6.62-6.98 (m, 24H), 7.71 (q, 1H, *J* = 8 Hz), 8.39 (d, 1H, *J* = 8Hz). Anal. Calcd for $C_{72}H_{90}N_2O_{16}\cdot 0.2CH_2Cl_2$: C, 69.01; H, 7.25; N, 2.23. Found: C, 68.67; H, 7.14; N, 2.62.

Bis(crown ether) ***24*** with mp 138-140 °C was realized in 53% yield: IR(deposit from CH_2Cl_2 solution on a NaCl plate): 3261 (NH), 1659 (C=O) cm^{-1}; ^1H NMR δ 0.84, (t, 6H, *J* = 6Hz), 1.19 (s, 20H), 1.50 (m, 4H), 1.88-1.95 (m, 4H), 2.17 (m, 2H), 3.73-3.85 (m, 8H), 4.01-4.19 (m, 16H), 4.29-4.64 (m, 8H), 6.67-6.99 (m, 24H), 7.63 (d, 2H, *J* = 8Hz). Anal. Calcd for $C_{73}H_{92}N_2O_{16}$: C, 69.94; H, 7.39; N, 2.24. Found: C, 69.79; H, 7.66; N, 2.23.

Bis(crown ether) ***25*** with mp 138-140 °C was formed in 42% yield: IR(deposit from CH_2Cl_2 solution on a NaCl plate) 3366 (NH), 1674 (C=O) cm^{-1}; ^1H NMR δ 0.84 (t, 6H, *J* = 6Hz), 1.20 (s, 20H), 1.52 (m, 4H), 1.90-1.94 (m, 4H), 3.71-3.97 (m, 12H), 4.01-4.20 (m, 16H), 4.31-4.41 (m, 6H), 4.55-4.61 (m, 2H), 6.65-6.98 (m, 24H), 7.66 (d, 2H, *J* = 8 Hz). Anal. Calcd for $C_{74}H_{94}N_2O_{17}$: C, 69.24; H, 7.38; N, 2.19. Found: C, 68.89; H, 7.50; N, 2.25.

General Procedure for Preparation of Macrocyclic Polyether Diamides 26-32. A solution of the diamine (2.0 mmol) and Et_3N (4.0 mmol) in CH_2Cl_2 was added in one portion to a vigorously stirred solution of the diacid chloride (2.0 mmol, prepared from dicarboxylic acids **10-12** and **14** as described above) in CH_2Cl_2 (50 mL) at 0 °C. The reaction mixture was stirred at room temperature for 10-30 min and filtered. The filtrate washed with water, 10% aq NaOH and then again with water, dried over Na_2SO_4 and evaporated in vacuo. The crude solid product was purified by chromatography on silica gel with CH_2Cl_2-MeOH (9:1) as eluent.

1,17-Diaza-5,6,12,13-dibenzo-3,15-ditetradecane-4,7,11,14-tetraoxacyclononadecane-2,16-dione (**26**) with mp 102-104 °C was obtained from **10** and **43a** in 85% yield after recrystallization from *n*-hexane; IR (KBr) 3360 (NH), 1662 (C=O) cm^{-1}; ^1H NMR δ 0.84 (t, 6H, J = 6 Hz), 1.22 (s, 44H), 1.14-2.21 (m, 8H), 3.34-3.47 (m, 4H), 4.24-4.58 (m, 8H), 6.65-6.95 (m, 8H), 7.62 (br s, 2H, NH); MS: m/z = 793 (M^+). Anal. Calcd for $C_{49}H_{80}N_2O_6\bullet 1.5H_2O$: C, 71.75; H, 10.20; N, 3.41. Found: C, 71.87; H, 9.87; N, 3.38.

1,17-Diaza-5,6,12,13-dibenzo-3,15-ditetradecane-4,7,11,14-tetraoxacycloeicosane-2,16-dione (**27**) with mp 78-80 °C was isolated from **10** and **43b** in 89% yield; IR (KBr) 3357 (NH), 1658 (C=O) cm^{-1}; ^1H NMR δ 0.84 (t, 6H, J = 6 Hz), 1.22 (s, 44H), 1.50-2.23 (m, 8H), 3.02-3.20 (m, 6H), 4.21-4.53 (m, 6H), 6.68-6.95 (m, 8H), 7.98 (br s, 2H, NH); MS: m/z = 807 (M^+). Anal. Calcd for $C_{50}H_{82}N_2O_6\bullet 0.5H_2O$: C, 73.57; H, 10.25; N, 3.43. Found: C, 73.54; H, 10.11; N, 3.15.

1,19-Diaza-5,6,14,15-dibenzo-4,7,10,13,15-pentaoxacyclouneicosane-2,18-dione (**28**) with mp 156-158 °C was obtained from **11** and **43a** in 93% yield: IR (KBr) 3340 (NH), 1678 C=O cm^{-1}; ^1H NMR δ 3.35-3.55 (m, 4H), 3.98-4.24 (m, 8H), 4.53 (s, 4H), 6.90-7.00 (m, 8H), 7.90 (br s, 2H, NH); MS: m/z = 430 (M^+). Anal. Calcd for $C_{22}H_{26}N_2O_7\bullet 1.25H_2O$: C, 58.33; H, 6.34; N, 6.18. Found: C, 58.42; H, 6.67, N, 6.16.

1,19-Diaza-5,6,14,15-bis(-4'(5')-tert-butyldibenzo-4,7,10,13,15-pentaoxacyclouneicosane-2,18-dione (**29**) with mp 133-135 °C was produced from **12** and **43a** in 93% yield: IR (KBr) 3358 (NH), 1678 (C=O) cm^{-1}; ^1H NMR δ 1.25 (s, 18H), 3.41-3.53 (m, 4H), 3.94-4.52 (m, 10H), 6.79-6.98 (m, 6H), 7.93 (br s, 2H, NH): MS: m/z = 542 (M^+). Anal. Calcd for $C_{30}H_{42}N_2O_7\bullet 0.5H_2O$: C, 65.32; H, 7.85; N, 5.08. Found: C, 65.52; H, 7.64; N, 4.90.

1,19-Diaza-5,6,14,15-dibenzo-3,17-ditetradecane-4,7,10,13,15-pentaoxacyclouneicosane-2,18-dione (**30**) with mp 75-77 °C was obtained from **14** and **43a** in 80% yield after recrystallization from *n*-hexane; IR (KBr) 3367 (NH), 1678 (C=O) cm^{-1}; ^1H NMR δ 0.84 (t, 6H, J = 6 Hz), 1.22 (s, 44H), 1.48-1.88 (m, 8H), 3.18-3.40 (m, 4H), 3.91-4.47 (m, 10H), 6.89-6.93 (m, 8H), 7.70 (br s, 2H, NH); MS: m/z = 823 (M^+). Anal. Calcd for $C_{50}H_{82}N_2O_7$: C, 72.95; H, 10.04; N, 3.40. Found: C, 73.16; H, 10.14; N, 3.36.

1,19-Diaza-5,6,14,15-dibenzo-3,17-ditetradecane-4,7,10,13,15-pentaoxacyclodocosane-2,18-dione (**31**) with mp 94-96 °C was produced from **14** and **43b** in 90% yield: IR(KBr) 3309 (NH), 1651 (C=O) cm^{-1}; ^1H NMR δ

0.84 (t, 6H, $J = 6$ Hz), 1.23 (s, 44H), 1.46-1.98 (m, 8H), 3.18-3.38 (m, 6H), 3.87-4.61 (m, 10H), 6.88-6.95 (m, 8H), 7.70 (br s, 2H, NH); MS: m/z = 837 (M^+). Anal. Calcd for $C_{51}H_{84}N_2O_7$: C, 73.16; H, 10.11; N, 3.35. Found: C, 73.20; H, 10.14; N, 3.33.

1,19-Diaza-5,6,14,15,20,21-tribenzo-3,17-ditetradecane-4,7,10,13,15-pentaoxacyclouneicosane (**32**) was obtained from **14** and **43c** in 86% yield as an oil which solidified on standing: IR (film) 3371, 3309 (NH), 1689 (C=O) cm^{-1}; ^{1}H NMR δ 0.85 (t, 6H, $J = 6$ Hz), 1.23 (s, 44H), 1.26-1.85 (m, 8H), 3.68-4.44 (m, 10H), 6.79-7.63 (m, 12H), 9.29 (br s, 2H, NH); MS: m/z = 871 (M^+). Anal. Calcd for $C_{54}H_{82}N_2O_7$: C, 74.44; H, 9.49; N, 3.20. Found: C, 74.34; H, 9.11; N, 3.24.

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