Upper Rim Diester-bridged Calix[4]arenes and Oligocalix[4]-arenes: the Effects of the Length of Bridged Reagents on Their Distribution

ZENG, Cheng-Chu(曾程初) **YUAN, Hu-Shan**(原虎山) **HUANG, Zhi-Tang***(黄志镗)
Center for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

A series of monobridged calix[4]arenes 3a—f, cyclic biscalix[4]arenes 4a—f, diametrically bridged at the upper rim with saturated aliphatic diester chains, have been synthesized. The results at dilute conditions show that the percentage of yields of mono-, bis- and oligo-calix[4]arenes are related to the length of the chains. With the shortening of the chains, the percentage of monocalix[4]arenes decreased. All the calix[4]arene moieties are in a cone conformation according to the AB quartet pattern of the methylene protons between the phenolic rings in the ^{1}H NMR spectra.

Keywords calixarene, monobridged calixarene, biscalixarene, host molecules

Introduction

Calix[4]arenes have been attracting much attention in the last few decades because of their simple one-pot preparation and the unique structural properties.[1] They have been used as useful building blocks for larger and more sophisticated molecular systems in supramolecular chemistry. The well-preorganization together with the simple chemical derivatization of a calix[4]arene makes the molecule especially useful in the design and synthesis of a wide range of receptor with recognition ability towards both neutral and charged molecule.[2] Although the earlier attention has been paid mostly to the monocalix[4]-arenes, increasing interest is being directed to the more elaborated structures consisting of multiple calix[4]arenes with designed cavities and networks.[3] Since each calix[4]arene can act as one recognition site, such multiple calix[4]arenes assemblies can lead to a novel receptor systems with multi-point recognition sites possessing new building properties unknown in mono-calix[4]arene.[3f] A possible approach to achieve this aim seems to be the connection of bridged reagents employing α, ω-difunctional groups with appropriate difunctional derivatives of calix[4]arene borne at the upper rim or the lower rim of calix[4]arenes. In general, due to the possibility of intra-versus inter-molecular reaction three types of products, monobridged calix[4]arene, cyclic biscalix[4]arene and calix[4]arene oligomer, may be produced. In the past decade, many studies on the syntheses of these multiple calix[4]arenes and their complexation properties have been reported. For example, calix[4]arene has been bridged with poly(oxyethylene) chain,[4] aromatic moieties,[3c] and a ferrocene unit[5] at the lower rim. On the other hand, a series of upper rim bridged calix[4]arenes with rigid units, such as alkenyl,[3g] 2,4-hexadiynyl,[6] aromatic ring[7] and upper rim-upper rim oligo-calix[4]-arenes[3i,8] were synthesized. The properties of the bridged reagent, such as length, rigidity, may affect the distribution of the above-mentioned three types of products. However, to the best of our knowledge, no works have been reported in that connection. In this paper, syntheses of calix[4]arene derivatives with upper rim diametrically substituent and their effect on the distribution of the products via the intra- and inter-molecular reactions with the changing of length and rigidity of the bridged reagents were investigated. For this purpose, the aliphatic diacyl chlorides were chosen as the bridged reagents, in which length of the chain and its rigidity were changeable and, 5,17-bis(hydroxymethyl)-25,26,27,28-tetrakis(2′-ethoxy-

* E-mail: huangzt@public.bta.net.cn; Fax: 86-10-62559373
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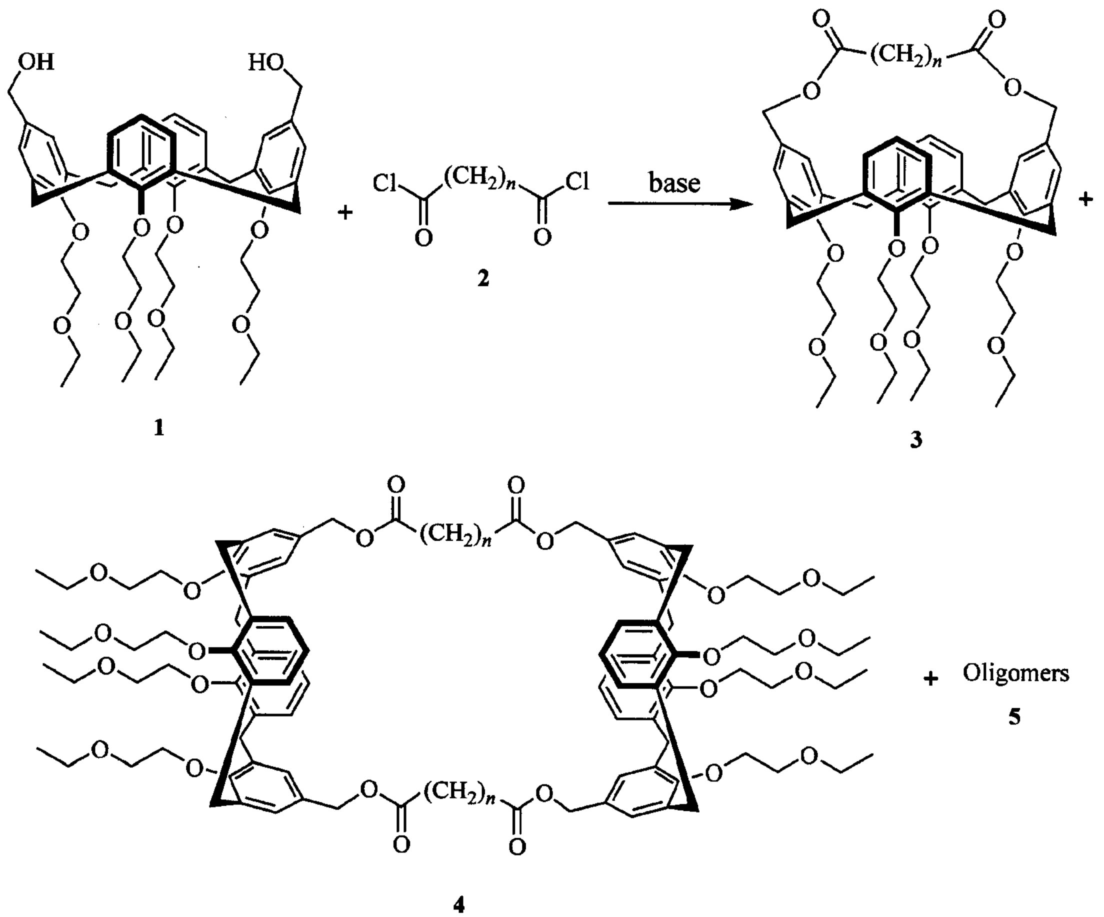
ethoxy)calix[4]arene (**1**) was selected to react with the aliphatic diacyl chlorides. To make the synthesis procedure and the spectroscopic analysis as simple as possible, the use of **1**, in which the calix[4]arene was alkylated at the lower rim with ethoxyethyl group, was intended for restricting the calix[4]arene moiety in cone conformation and for increasing the solubility in the appropriate solvents.[9]

Results and discussion

When the calix[4]arenediol **1** reacted with diacyl chlorides **2** in the presence of a base, the products were separated by column chromatography into three fractions in general. The first two were pure compounds, namely monobridged calix[4]arene **3** formed through the intramolecular condensation and cyclic biscalix[4]arene **4** formed through the intermolecular condensation. The third was a mixture of oligomers, called oligocalix[4]arene **5**, which were produced also through the intermolecular condensation. The total isolated yield of these three fractions was over 80%. The products were also analyzed by HPLC of a Zoebax SB-18 column at room temperature. The retention times of compounds **3** and **4** were compared with those of the pure compounds obtained by column chromatograph. The diacyl chlorides used are with different chain lengths ranging between the two carboxylic groups from one to eight methylene units. Terephthalyl chloride with a *p*-phenylene group was also used as comparison. The reaction is illustrated in Scheme 1.

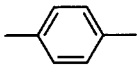
At first, the reaction was carried out in the presence of pyridine as a base at dilute conditions, *i.e.* 0.2 mmol of **1** in 80 mL of methylene chloride. The yields of monobridged calix[4]arene **3**, cyclic biscalix[4]arene **4** and oligocalix[4]arene **5** are listed in Table 1.

Scheme 1 Reaction of calix[4]arenediol **1** with diacyl chlorides



a, $n = 1$; **b**, $n = 2$; **c**, $n = 3$; **d**, $n = 4$; **e**, $n = 6$; **f**, $n = 8$; **g**,

Table 1 Yields (%) of **3**—**5**

2	n	Monobridg edcalix[4]arene 3		Cyclic bis- calix[4]arene 4		Oligo-calix[4]arene 5	
		Isolated[a]	HPLC	Isolated[a]	HPLC	Isolated[a]	HPLC
2a	1	34.5 (39.2)	55.6	0	2.4	53.6 (60.8)	41.0
2b	2	31.4 (37.3)	39.8	14.0 (16.6)	17.4	38.7 (46.0)	42.8
2c	3	37.4 (42.4)	41.3	21.9 (24.9)	23.7	28.8 (32.7)	35.0
2d	4	40.3 (47.3)	42.2	19.3 (22.7)	25.5	25.5 (30.0)	32.3
2e	6	63.7 (65.1)	66.5	0	0	34.1 (34.9)	33.5
2f	8	73.6 (78.9)	82.2	0	0	19.7 (21.1)	17.8
2g		0		34.5 (43.2)		45.4 (56.8)	

[a]The value in parentheses is calculated on the basis of 100%.

The structures of compounds **3** and **4** were determined by elemental analyses, ^{1}H NMR, ^{13}C NMR and IR spectra, especially by mass spectra. The ^{1}H NMR and ^{13}C NMR spectra were simplified due to the compounds **3** and **4** existing in C_2 symmetry. It is difficult to differentiate the structures of **3** and **4** by NMR spectra because their spectra were very similar. However, **3** and **4** could be easily distinguished by MALDI-TOF mass data. A low yield (4%) of a third compound **6** was isolated from the oligocalix[4]arene **5d** and it's ^{1}H NMR and ^{13}C NMR were also similar to those of **3d** and **4d**. Similarly, it could be confirmed by the MALDI-TOF mass data as a cyclic tricalix[4]arene as shown in Fig. 1. The AB quartet pattern of the methylene protons between the phenolic rings in the ^{1}H NMR spectra of **3**, **4** and **6** indicates that the calix[4]arene moieties retain their cone conformation as the raw material calix[4]arenediol **1**.

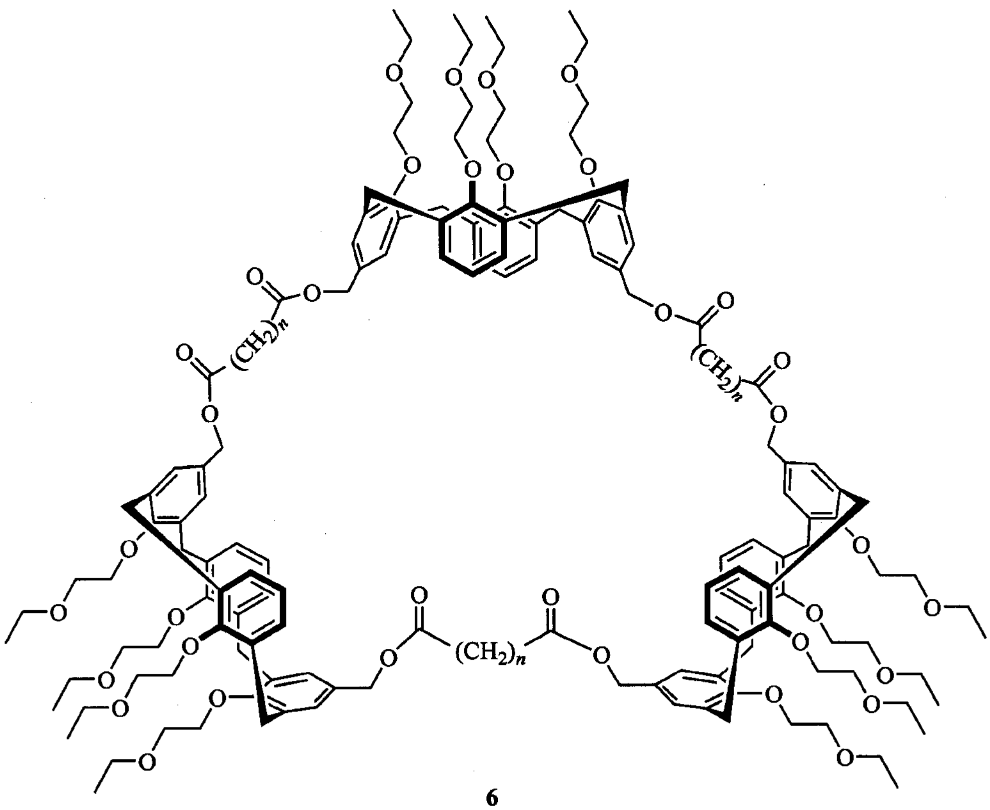


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Fig. 1 Structure of tricalix[6]arene **6**.

From the data of Table 1, it can be seen that the isolated yields and the yields analyzed by HPLC can be comparable and are certificated on each other. The monobridged calix[4]arene **3**, the product of intramolecular cyclization, was always the dominant fraction in the dilute conditions and increased gradually from *ca*. 30% to *ca*. 70% with the increase of chain length of diacid chloride from one to eight methylene units. This may be due to the more flexible of the chain of the diacyl chloride. When malonyl chloride (**2a**, $n = 1$) was used as bridged reagent to react with **1** under this condition, no cyclic biscalix[4]arene **4a** was isolated. As the chain length of the diacyl chlorides **2b**—**d** ($n = 2$—4) was increased, the cyclic biscalix[4]arenes **4b**—**d** were isolated in yields around 20%. When the chain length was longer ($n = 6$, 8), no more cyclic biscalix[4]arenes **4e** and**4f** were isolated, due to the high yields of the monobridged calix[4]arenes **3e** and **3f**. No obvious solvent effect was observed in the reaction of calix[4]arenediol **1** with **2d** when the reaction was carried out in methylene chloride, chloroform, benzene or acetonitrile. For comparison, terephthalyl chloride (**2g**) was used instead of aliphatic diacyl chlorides. In this case, only cyclic biscalix[4]arene **4g** could be found. It may be too rigid of the chain of the *p*-phenylene unit.

Brittain *et al*. have developed a method to prepare low molecular weight cyclic ester oligomers in high yields at more concentrated conditions by using appropriate base.[10] Accordingly, we carried out the above-mentioned reaction at more concentrated conditions (0.4 mmol of **1** in 20 mL of methylenechloride) in the presence of triethylamine and DABCO. The results are listed in Table 2.

Table 2 Isolated yields of **3**—**5** in more concentrated conditions

2	**1** recovered	**3**	**4**	**5**
2a	4.5	25.9	5.1	26.5
2b	13.9	8.5	0	64.1
2c	3.9	15.0	1.9	63.5
2d	1.0	15.0	1.4	66.9
2e	6.5	8.2	5.0	72.0
2f	8.4	42.9	5.3	35.3

From the data of Table 2, the higher yield of monobridged calix[4]arenes **3** and cyclic biscalix[4]arenes **4** can not be obtained, but an increasing of the yield of oligocalix[4]arenes **5** can be inferred. What is interesting is that from the mixture of products, low yields of new cyclic biscalix[4]arene **4a**, **4e** and **4f** could be isolated.

Conclusions

In summary, our syntheses of a series of capped monocalix[4]arenes and cyclic biscalix[4]arenes, diametrically bridged at the upper rim with aliphatic diester chains with different methylene units were successful and indicated that the product distribution of the intra- and inter-molecular reaction was related to the length of the bridged reagent at dilute conditions. All compounds were characterized by microanalysis, ^{1}H NMR, ^{13}C NMR, IR and MS spectra. Further investigation on the molecular recognition properties is in progress.

Experimental

Calix[4]arenediol **1** was prepared according to the reported procedures.[9,11] Melting points are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were obtained in $CDCl_3$ with Me_4Si as internal standard on a Bruker DMX 300 NMR spectrometer unless otherwise indicated. MALDI-TOF (matrix-assisted laser desorption ionization time-of-flight) mass spectra were recorded on a Bruker BIFLEX III spectrometer with the use of CCA (2-cyano-4′-hydroxycinnamic acid) as matrix. Microanalytical samples were dried at least 20 d at 80 ℃ under reduced pressure, and the analyses were carried out by the Analytical Laboratory of the Institute of Chemistry.

General procedure for the reaction of calix[4]arenediol **1** *with diacyl chlorides* **2a**—**g** *under dilute conditions*

A solution of diacyl chloride **2** (0.3 mmol) in 15 mL of CH_2Cl_2 and a solution of calix[4]arenediol **1** (155 mg, 0.2 mmol) in 15 mL of CH_2Cl_2 were added simultaneously at room temperature with two dropping funnels to a vigorously stirred solution of 0.6 mmol of pyridine in 50 mL of CH_2Cl_2. The addition was completed in 24 h, then the solution was stirred for a further 24 h and quenched with water (20 mL). The organic layer was washed with saturated $NaHCO_3$ solution (2 × 20 mL), distilled water (2 × 20 mL), dried over Na_2SO_4, evaporated under reduced pressure. Purification of the yellow residue by silica gel column chromatograph eluting with a mixture of petroleum ether (60—90 ℃) and ethyl acetate with a gradual increase of ethyl acetate afforded the corresponding products as white solid or oil.

Monocalix[4]*arene malonate* **3a** Yield 34.5%; m.p. 138—139 ℃; ^{1}H NMR ($CDCl_3$) δ: 1.18 (t, J=6.9 Hz, 6H, OCH_2**CH_3**), 1.25 (t, J=6.9 Hz, 6H, OCH_2**CH_3**), 3.15 (d, J = 12.9 Hz, 4H, Ar**CH_2**Ar), 3.19 (s, 2H, $COCH_2CO$), 3.54 (q, J= 6.9 Hz, 4H, O**CH_2**CH_3), 3.56 (q, J=6.9 Hz, 4H, O**CH_2**CH_3), 3.80 (t, J=4.9 Hz, 4H, OCH_2CH_2O), 3.92 (t, J=4.9 Hz, 4H, OCH_2CH_2O), 3.98 (t, J= 6.5 Hz, 4H, OCH_2CH_2O), 4.37 (t, J=6.5 Hz, 4H, OCH_2CH_2O), 4.51 (d, J=12.9 Hz, 4H, Ar**CH_2**Ar), 4.60 (s, 4H, Ar**CH_2**O), 6.37 (s, 4H, Ar**H**), 6.94 (t, J=7.5 Hz, 2H, Ar**H**), 7.13 (d, J=7.5 Hz, 4H, Ar**H**); ^{13}C NMR ($CDCl_3$) δ: 15.0, 15.2, 30.5, 42.0, 66.1, 66.4, 66.6, 69.4, 69.5, 72.0, 74.1, 122.5, 128.6, 128.6, 128.7, 133.0, 135.9, 154.5, 157.1, 166.0; IR (KBr) ν: 1748, 1726 (C=O) cm^{-1}; MS (MALDI-TOF) m/z: 863.20 $(M+Na)^+$, 879.20 $(M+K)^+$. Anal. calcd for $C_{49}H_{60}O_{12}$: C 69.98, H 7.19; found C 70.39, H 7.23.

Monocalix[4]*arene succinate* **3b** Yield 31.4%; m.p. 98—99 ℃; ^{1}H NMR ($CDCl_3$) δ: 1.20 (t, J= 6.9 Hz, 6H, OCH_2**CH_3**), 1.27 (t, J=6.9 Hz, 6H, OCH_2**CH_3**), 2.49 (s, 4H, $COCH_2CH_2CO$), 3.16 (d, J=12.9 Hz, 4H, Ar**CH_2**Ar), 3.55 (q, J=6.9 Hz, 4H, O**CH_2**CH_3), 3.61 (q, J = 6.9 Hz, 4H, O**CH_2**CH_3), 3.81 (t, J=4.5 Hz, 4H, OCH_2CH_2O), 3.95 (t, J=4.5 Hz, 4H, OCH_2CH_2O), 4.00 (t, J= 6.3 Hz, 4H, OCH_2CH_2O), 4.37 (t, J=6.3 Hz, 4H, OCH_2CH_2O), 4.53 (d, J=12.9 Hz, 4H, Ar**CH_2**Ar), 4.60 (s, 4H, Ar**CH_2**O), 6.29 (s, 4H, Ar**H**), 6.96 (t, J=7.3 Hz, 2H, Ar**H**), 7.15 (d, J=7.3 Hz, 4H, Ar**H**); ^{13}C NMR ($CDCl_3$) δ: 15.2, 15.3, 29.8, 30.7, 65.5, 66.2, 66.5, 69.6, 69.6, 72.2, 74.2, 122.4, 126.1, 128.8, 129.4, 133.0, 136.3, 154.3, 157.5, 171.7; IR (KBr) ν: 1725 (C=O) cm^{-1}; MS (MALDI-TOF) m/z: 877.35 $(M+Na)^+$, 893.32 $(M+K)^+$. Anal. calcd for $C_{50}H_{62}O_{12}$: C 70.23, H 7.31; found C 70.53, H 7.53.

Biscalix[4]*arene succinate* **4b** Yield 14.0%; m.p. 125—126 ℃; ^{1}H NMR ($CDCl_3$) δ: 1.18 (t, J=6.9 Hz, 12H, OCH_2**CH_3**), 1.25 (t, J=6.9 Hz, 12H, OCH_2**CH_3**), 2.46 (s, 8H, $COCH_2CH_2CO$), 3.12 (d, J=13.5 Hz, 8H, Ar**CH_2**Ar), 3.52 (q, J= 6.9 Hz, 8H, O**CH_2**CH_3), 3.59 (q, J=6.9 Hz, 8H, O**CH_2**CH_3), 3.80 (t, J=4.5 Hz, 8H, OCH_2CH_2O), 3.92 (t, J=4.5 Hz, 8H, OCH_2CH_2O), 3.95 (t, J= 6.3 Hz, 8H, OCH_2CH_2O), 4.30 (t, J=6.3 Hz, 8H, OCH_2CH_2O), 4.50 (d, J=13.5 Hz, 8H, Ar**CH_2**Ar), 4.53 (s, 8H, Ar**CH_2**O), 6.19 (s, 8H, Ar**H**), 6.88 (t, J=7.3 Hz, 4H, Ar**H**), 7.02 (d, J=7.3 Hz, 8H, Ar**H**); ^{13}C NMR ($CDCl_3$) δ: 15.0, 15.1, 28.9, 30.6, 66.0, 66.3, 66.3, 69.4, 69.5, 72.2, 73.7, 122.2, 127.0, 128.7, 129.0, 133.4, 136.1, 154.6, 157.4, 171.9; IR (KBr) ν: 1737 (C=10) cm^{-1}; MS (MALDI-TOF) m/z: 1731.57 $(M+Na)^+$, 1747.55 $(M+K)^+$ Anal. calcd for $C_{100}H_{124}O_{24}$: C 70.23, H 7.31; found C 70.19, H 7.40.

Monocalix[4]*arene glutarate* **3c** Yield 37.4%; m.p. 90—91 ℃; ^{1}H NMR ($CDCl_3$) δ: 1.20 (t, J= 6.9 Hz, 6H, OCH_2**CH_3**), 1.27 (t, J=6.9 Hz, 6H, OCH_2**CH_3**), 1.92 (quin, J=6.1 Hz, 2H, CH_2**CH_2**CH_2), 2.33 (t, J=6.1 Hz, 4H, **CH_2**CH_2**CH_2**), 3.16 (d, J=13.2 Hz, 4H, Ar**CH_2**Ar), 3.57 (q, J=6.9 Hz, 4H, O**CH_2**CH_3), 3.58 (q, J = 6.9 Hz, 4H, O**CH_2**CH_3), 3.79 (t, J=4.8 Hz, 4H, OCH_2CH_2O), 3.94 (t, J=4.8 Hz, 4H, OCH_2CH_2O), 3.97 (t, J= 6.3Hz, 4H, OCH_2CH_2O), 4.35 (t, J=6.3 Hz, 4H, OCH_2CH_2O), 4.51 (d, J=13.2 Hz, 4H, Ar**CH_2**Ar), 4.57 (s, 4H, Ar**CH_2**O), 6.21 (s, 4H, Ar**H**), 6.95 (t, J=7.2 Hz, 2H, Ar**H**), 7.15 (d, J=7.2 Hz, 4H, Ar**H**); ^{13}C NMR ($CDCl_3$) δ: 15.0, 15.2, 20.1, 30.6, 34.3, 64.5, 66.0, 66.3, 69.4, 69.5, 72.1, 74.0, 122.0, 124.8, 128.7, 129.1, 133.1, 136.3, 153.8, 157.5, 172.3; IR (KBr) ν: 1744 (C=O) cm^{-1}; MS (MALDI-TOF) m/z: 891.27 $(M+Na)^+$, 907.23 $(M+K)^+$. Anal. calcd for $C_{51}H_{64}O_{12}$: C 70.48, H 7.42; found C 70.41, H 7.55.

Biscalix[4]*arene glutarate* **4c** Yield 21.9%; m.p. 38—40 ℃; ^{1}H NMR ($CDCl_3$) δ: 1.17 (t, J= 6.9 Hz, 12H, OCH_2**CH_3**), 1.24 (t, J = 6.9 Hz, 12H, OCH_2**CH_3**), 1.82 (t, J=7.2 Hz, 4H, CH_2**CH_2**CH_2), 2.29 (t, J=7.2 Hz, 8H, **CH_2**CH_2**CH_2**), 3.11 (d, J=13.2 Hz, 8H, Ar**CH_2**Ar), 3.53 (q, J= 6.9 Hz, 8H, O**CH_2**CH_3), 3.55 (q, J=6.9 Hz, 8H, O**CH_2**CH_3), 3.81 (t, J=4.9 Hz, 8H, OCH_2CH_2O), 3.89 (t, J=4.9 Hz, 8H, OCH_2CH_2O), 3.97 (t, J= 5.8 Hz, 8H, OCH_2CH_2O), 4.26 (t, J=5.8 Hz, 8H, OCH_2CH_2O), 4.48 (d, J=13.2 Hz, 8H, Ar**CH_2**Ar), 4.57 (s, 8H, Ar**CH_2**O), 6.23 (s, 8H, Ar**H**), 6.80 (t, J=7.5 Hz, 4H, Ar**H**), 6.93 (d, 8H, J=7.5

Hz, Ar**H**); ^{13}C NMR ($CDCl_3$) δ: 15.3, 15.3, 20.0, 30.8, 33.2, 65.7, 66.2, 66.5, 69.7, 69.7, 72.6, 73.8, 122.3, 127.3, 128.7, 129.5, 133.9, 136.0, 155.1, 157.4, 172.7; IR (KBr) ν: 1736 (C = O) cm^{-1}; MS (MALDI-TOF) m/z: 1759.34 $(M+Na)^+$, 1775.29 $(M+K)^+$. Anal. calcd for $C_{102}H_{128}O_{24}$: C 70.48, H 7.42; found C 70.38, H 7.45.

Monocalix[4]*arene adipate* **3d** Yield 40.3%; m.p. 60—61 ℃; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 1.18 (t, J=7.0 Hz, 6H, OCH_2CH_3), 1.25 (t, J= 7.0 Hz, 6H, OCH_2CH_3), 1.57 (quin, J = 3.0 Hz, 4H, $CH_2(CH_2)_2CH_2$), 2.24 (t, J=3.0 Hz, 4H, CH_2-$(CH_2)_2CH_2$), 3.15 (d, J = 12.9 Hz, 4H, $ArCH_2Ar$), 3.53 (q, J=7.0 Hz, 4H, OCH_2CH_3), 3.58 (q, J= 7.0 Hz, 4H, OCH_2CH_3), 3.77 (t, J = 3.0 Hz, 4H, OCH_2CH_2O), 3.91 (t, J=3.0 Hz, 4H, OCH_2CH_2O), 3.98 (t, J=6.9 Hz, 4H, OCH_2CH_2O), 4.36 (t, J= 6.9 Hz, 4H, OCH_2CH_2O), 4.51 (d, J = 13.2 Hz, 4H, $ArCH_2Ar$), 4.67 (s, 4H, $ArCH_2O$), 6.28 (s, 4H, Ar**H**), 6.90 (t, J = 7.2 Hz, 2H, Ar**H**), 7.12 (d, J = 7.2 Hz, 4H, Ar**H**); ^{13}C NMR ($CDCl_3$) δ: 15.2, 15.3, 23.6, 30.8, 33.0, 64.7, 66.2, 66.5, 69.5, 69.6, 72.2, 74.3, 122.5, 125.4, 128.7, 129.8, 133.1, 136.4, 154.0, 157.4, 173.2; IR (KBr) ν: 1742, 1715 (C = O) cm^{-1}; MS (MALDI-TOF) m/z: 905.31 $(M+Na)^+$, 921.29 $(M+K)^+$. Anal. calcd for $C_{52}H_{66}O_{12}$: C 70.72, H 7.53; found C 70.62, H 7.68.

Biscalix[4]*arene adipate* **4d** Yield 19.3%; m.p. 144—145 ℃; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 1.18 (t, J=6.9 Hz, 12H, OCH_2CH_3), 1.25 (t, J= 6.9 Hz, 12H, OCH_2CH_3), 1.57 (quin, J = 4.5 Hz, 8H, $CH_2(CH_2)_2CH_2$), 2.25 (t, J = 4.5 Hz, 8H, CH_2-$(CH_2)_2CH_2$), 3.15 (d, J = 12.9 Hz, 8H, $ArCH_2Ar$), 3.53 (q, J = 6.9 Hz, 8H, OCH_2CH_3), 3.58 (q, J = 6.9 Hz, 8H, OCH_2CH_3), 3.77 (t, J = 4.4 Hz, 8H, OCH_2CH_2O), 3.93 (t, J = 4.4 Hz, 8H, OCH_2CH_2O), 3.99 (t, J = 6.3 Hz, 8H, OCH_2CH_2O), 4.36 (t, J= 6.3 Hz, 8H, OCH_2CH_2O), 4.51 (d, J = 12.9 Hz, 8H, $ArCH_2Ar$), 4.67 (s, 8H, $ArCH_2O$), 6.28 (s, 8H, Ar**H**), 6.90 (t, J = 7.4 Hz, 4H, Ar**H**), 7.12 (d, J = 7.35 Hz, 8H, Ar**H**); ^{13}C NMR ($CDCl_3$) δ: 15.0, 15.2, 23.4, 30.6, 32.8, 64.5, 66.0, 66.3, 69.3, 69.5, 72.0, 74.1, 122.3, 125.2, 128.5, 129.6, 132.9, 136.2, 153.9, 157.2, 173.1; IR (KBr) ν: 1732 (C = O) cm^{-1}; MS (MALDI-TOF) m/z: 1787.84 $(M+Na)^+$, 1803.83 $(M+K)^+$. Anal. calcd for $C_{104}H_{132}O_{24}$: C 70.72, H 7.53; found C 70.42, H 7.34.

Tricalix [4] *arene adipate* **6** Yield 4.0%; m.p. 76—78 ℃; ^{1}H NMR ($CDCl_3$) δ: 1.18 (t, J = 7.5 Hz, 18H, OCH_2CH_3), 1.23 (t, J = 7.5 Hz, 18H, OCH_2CH_3), 1.61 (quin, J = 4.5 Hz, 12H, CH_2-$(CH_2)_2CH_2$), 2.29 (t, J = 4.5 Hz, 12H, CH_2-$(CH_2)_2CH_2$), 3.12 (d, J = 13.4 Hz, 12H, $ArCH_2Ar$), 3.52 (q, J = 7.5 Hz, 12H, OCH_2CH_3), 3.54 (q, J = 7.5 Hz, 12H, OCH_2CH_3), 3.81 (t, J = 5.4 Hz, 12H, OCH_2CH_2O), 3.85 (t, J = 5.9 Hz, 12H, OCH_2CH_2O), 4.03 (t, J = 5.4 Hz, 12H, OCH_2-CH_2O), 4.16 (t, J = 5.9 Hz, 12H, OCH_2CH_2O), 4.47 (d, J = 13.4 Hz, 12H, $ArCH_2Ar$), 4.65 (s, 12H, $ArCH_2O$), 6.42 (s, 12H, Ar**H**), 6.67 (t, J = 7.3 Hz, 6H, Ar**H**), 6.75 (d, J = 7.3 Hz, 12H, Ar**H**); ^{13}C NMR ($CDCl_3$) δ: 15.2, 15.2, 24.3, 30.8, 33.8, 66.3, 66.3, 66.5, 69.6, 69.7, 73.7, 122.3, 127.4, 128.5, 129.4, 134.0, 135.9, 155.2, 157.2, 173.1; IR (KBr) ν: 1732 (C = O) cm^{-1}; MS (MALDI-TOF) m/z: 2670.4 $(M+Na)^+$, 2686.4 $(M+K)^+$. Anal. calcd for $C_{156}H_{198}O_{36}$: C 70.72, H 7.53; found C 70.68, H 7.59.

Monocalix[4]*arene suberate* **3e** Yield 63.7%; m.p. 81—82 ℃; ^{1}H NMR ($CDCl_3$) δ: 1.22 (t, J = 6.9 Hz, 6H, OCH_2CH_3), 1.26 (t, J = 6.9 Hz, 6H, OCH_2CH_3), 1.20—1.30 (m, 4H, $CH_2(CH_2)_4CH_2$), 1.42—1.50 (m, 4H, $CH_2(CH_2)_4CH_2$), 2.25 (t, J = 6.9 Hz, 4H, $CH_2(CH_2)_4CH_2$), 3.17 (d, J = 12.9 Hz, 4H, $ArCH_2Ar$), 3.53 (q, J = 6.9 Hz, 4H, OCH_2CH_3), 3.62 (q, J = 6.9 Hz, 4H, OCH_2CH_3), 3.89 (t, J = 3.6 Hz, 4H, OCH_2CH_2O), 3.90 (t, J = 3.6 Hz, 4H, OCH_2CH_2O), 4.06 (t, J = 5.4 Hz, 4H, OCH_2CH_2O), 4.20 (t, J = 5.4 Hz, 4H, OCH_2CH_2O), 4.51 (d, J = 12.9 Hz, 4H, $ArCH_2Ar$), 4.74 (s, 4H, $ArCH_2O$), 6.55 (s, 4H, Ar**H**), 6.72 (t, J = 7.4 Hz, 2H, Ar**H**), 6.93 (d, 4H, J = 7.4 Hz, Ar**H**); ^{13}C NMR ($CDCl_3$) δ: 15.3, 15.3, 24.2, 28.1, 30.5, 34.5, 65.5, 66.3, 66.4, 66.5, 69.6, 73.0, 73.5, 122.4, 127.5, 128.5, 130.1, 134.3, 135.2, 155.1, 156.4, 173.4; IR (KBr) ν: 1731 (C = O) cm^{-1}; MS (MALDI-TOF) m/z: 933.51 $(M+Na)^+$, 949.49 $(M+K)^+$. Anal. calcd for $C_{54}H_{70}O_{12}$: C 71.18, H 7.74; found C 71.06, H 7.91.

Monocalix[4]*arene sebacate* **3f** Yield 73.6%; m.p. 85℃; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 1.19 (t,

$J = 6.8$ Hz, 6H, OCH_2CH_3), 1.23 (t, $J = 6.8$ Hz, 6H, OCH_2CH_3), 1.10—1.18 (m, 8H, $CH_2(CH_2)_6$-CH_3), 1.40—1.48 (m, 4H, $CH_2(CH_2)_6$-CH_3), 2.24 (t, $J = 7.3$ Hz, 4H, $COCH_2$), 3.14 (d, $J = 12.9$ Hz, 4H, $ArCH_2Ar$), 3.56 (q, $J = 6.8$ Hz, 8H, OCH_2CH_3), 3.82 (t, $J = 5.3$ Hz, 4H, OCH_2CH_2O), 3.93 (t, $J = 6.0$ Hz, 4H, OCH_2CH_2O), 4.04 (t, $J = 5.29$ Hz, 4H, OCH_2CH_2O), 4.20 (t, $J = 6.0$ Hz, 4H, OCH_2CH_2O), 4.48 (d, $J = 12.9$ Hz, 4H, $ArCH_2Ar$), 4.90 (s, 4H, $ArCH_2O$), 6.40 (t, $J = 6.93$ Hz, 2H, ArH), 6.50 (d, $J = 6.93$ Hz, 4H, ArH), 6.89 (s, 4H, ArH); ^{13}C NMR ($CDCl_3$) δ: 15.2, 15.3, 25.2, 28.8, 29.0, 30.5, 35.1, 65.8, 66.3, 66.4, 69.6, 69.7, 72.8, 73.5, 122.3, 127.9, 129.7, 130.1, 134.6, 135.6, 155.3, 156.6, 173.6; IR (KBr) ν: 1733 (C=O) cm^{-1}; MS (MALDI-TOF) m/z: 961.47 $(M + Na)^+$, 977.41 $(M + K)^+$. Anal. calcd for $C_{56}H_{74}O_{12}$: C 71.61, H 7.94; found C 71.60, H 7.78.

Biscalix[4]*arene terephthalate* **4g** Owing to the lower solubility of terephthaloyl chloride in CH_2Cl_2, THF is used instead of CH_2Cl_2. Yield 34.5%; m.p. 278—279 ℃; ^{1}H NMR ($CDCl_3$) δ: 1.21 (t, $J = 6.9$ Hz, 12H, OCH_2CH_3), 1.27 (t, $J = 6.9$ Hz, 12H, OCH_2CH_3), 3.24 (d, $J = 13.4$ Hz, 8H, $ArCH_2Ar$), 3.56 (q, $J = 6.9$ Hz, 8H, OCH_2CH_3), 3.62 (q, $J = 6.9$ Hz, 8H, OCH_2CH_3), 3.84 (t, $J = 4.0$ Hz, 8H, OCH_2CH_2O), 3.95—4.05 (m, 16H, OCH_2CH_2O), 4.42 (t, $J = 6.0$ Hz, 8H, OCH_2CH_2O), 4.60 (s, 8H, $ArCH_2O$), 4.61 (d, $J = 13.4$ Hz, 8H, $ArCH_2Ar$), 6.34 (s, 8H, ArH), 7.00 (t, 4H, $J = 7.4$ Hz, ArH), 7.22 (d, $J = 7.4$ Hz, 8H, ArH), 7.65 (s, 8H, ArH); ^{13}C NMR ($CDCl_3$) δ: 15.2, 15.3, 30.9, 66.2, 66.3, 66.5, 69.6, 69.7, 72.4, 74.1, 122.5, 125.9, 128.9, 129.1, 129.2, 133.1, 133.5, 136.7, 154.4, 157.8, 164.7; IR (KBr) ν: 1726 (C = O) cm^{-1}; MS (MALDI-TOF) m/z: 1827.55 $(M + Na)^+$, 1843.50 $(M + K)^+$. Anal. calcd for $C_{108}H_{124}O_{24}$: C 71.82, H 6.92; found C 71.83, H 6.90.

General procedure for the reaction of calix[4]*arenediol* **1** *with diacyl chloride* **2a**—**f** *under more concentrated conditions*

A solution of calix[4]arenediol **1** (0.4 mmol) in 2 mL of CH_2Cl_2 and a solution of diacid chloride **2** (0.4 mmol) in 2 mL of CH_2Cl_2 were added dropwise simultaneously to a solution of 0.8 mmol of triethyleneamine and catalytic amounts (1 mg) of DABCO (1,4-diazabicyclo-[2,2,2]octane) in 16 mL of CH_2Cl_2. The reaction mixture was stirred for 36 h. Then the work-up was similar to the above-mentioned procedure at dilute conditions.

Biscalix[4]*arene malonate* **4a** Yield 5.1%; m.p. 48—50 ℃; ^{1}H NMR ($CDCl_3$) δ: 1.16 (t, $J = 6.9$ Hz, 12H, OCH_2CH_3), 1.21 (t, $J = 6.9$ Hz, 12H, OCH_2CH_3), 3.11 (d, $J = 13.2$ Hz, 8H, $ArCH_2Ar$), 3.21 (s, 4H, $COCH_2CO$), 3.47—3.56 (m, 16H, OCH_2CH_3), 3.78 (t, $J = 4.8$ Hz, 8H, OCH_2CH_2O), 3.87 (t, $J = 6.10$ Hz, 8H, OCH_2-CH_2O), 3.97 (t, $J = 4.8$ Hz, 8H, OCH_2CH_2O), 4.22 (t, $J = 6.10$ Hz, 8H, OCH_2CH_2O), 4.47 (d, $J = 13.2$ Hz, 4H, $ArCH_2Ar$), 4.60 (s, 8H, $ArCH_2O$), 6.25 (s, 8H, ArH), 6.75 (t, $J = 7.30$ Hz, 4H, ArH), 6.90 (d, $J = 7.30$ Hz, 8H, ArH); ^{13}C NMR ($CDCl_3$) δ: 15.2, 15.2, 30.6, 41.5, 66.1, 66.4, 66.6, 69.6, 69.6, .72.2, 73.7, 122.3, 127.3, 128.6, 128.7, 134.0, 135.7, 155.3, 157.0, 166.1; IR (KBr) ν: 1737 (C=O) cm^{-1}; MS (MALDI-TOF) m/z: 1702.82 $(M + Na)^+$, 1718.80 $(M + K)^+$. Anal. calcd for $C_{98}H_{120}O_{24}$: C 69.98, H 7.19; found C 70.22, H 7.44.

Biscalix[4]*arene suberate* **4e** Yield 5.0%; m.p. 38—40 ℃; ^{1}H NMR ($CDCl_3$) δ: 1.18 (t, $J = 6.9$ Hz, 12H, OCH_2CH_3), 1.22 (t, $J = 6.9$ Hz, 12H, OCH_2CH_3), 1.25—1.32 (m, 8H, $CH_2(CH_2)_4$-CH_2), 1.50—1.70 (m, 8H, $CH_2(CH_2)_4CH_2$), 2.25 (t, $J = 7.44$ Hz, 8H, $COCH_2$), 3.14 (d, $J = 13.2$ Hz, 8H, $ArCH_2Ar$), 3.51—3.57 (m, 16H, OCH_2CH_3), 3.81 (t, $J = 5.1$ Hz, 8H, OCH_2CH_2O), 3.88 (t, $J = 6.9$ Hz, 8H, OCH_2CH_2O), 4.00 (t, $J = 5.1$ Hz, 8H, OCH_2CH_2O), 4.21 (t, $J = 6.9$ Hz, 8H, OCH_2CH_2O), 4.49 (d, $J = 13.2$ Hz, 8H, $ArCH_2Ar$), 4.60 (s, 8H, $ArCH_2O$), 6.34 (s, 8H, ArH), 6.76 (t, $J = 7.2$ Hz, 4H, ArH), 6.87 (d, $J = 7.2$ Hz, 8H, ArH); ^{13}C NMR ($CDCl_3$) δ: 15.2, 15.3, 24.7, 28.7, 30.7, 34.1, 65.7, 66.2, 66.3, 66.4, 69.6, 73.2, 73.7, 122.4, 127.5, 128.5, 129.5, 134.2, 135.7, 155.4, 157.0, 173.3; IR (KBr) ν: 1736, 1725 (C=O) cm^{-1}; MS (MALDI-TOF) m/z: 1843.06 $(M + Na)^+$, 1859.01 $(M + K)^+$. Anal. calcd for $C_{108}H_{140}O_{24}$: C 71.18, H 7.74; found C 71.17, H

7.90.

Biscalix[4]*arene sebacate* **4f** Oil, yield 5.3%; ^{1}H NMR ($CDCl_3$) δ: 1.16—1.30 (m, 24H, OCH_2CH_3), 2.25 (t, J = 7.38 Hz, 8H, $COCH_2$), 3.13 (d, J = 13.4 Hz, 8H, $ArCH_2Ar$), 3.51—3.57 (m, 16H, OCH_2CH_3), 3.82 (t, J = 6.20 Hz, 8H, OCH_2CH_2O), 3.87 (t, J = 6.20 Hz, 8H, OCH_2CH_2O), 4.02 (t, J = 5.58 Hz, 8H, OCH_2CH_2O), 4.20 (t, J = 5.58 Hz, 8H, OCH_2CH_2O), 4.49 (d, J = 13.4 Hz, 8H, $ArCH_2Ar$), 4.63 (s, 8H, $ArCH_2O$), 6.36 (s, 8H, ArH), 6.73 (t, J = 7.35 Hz, 4H, ArH), 6.84 (d, J = 7.35 Hz, 8H, ArH); ^{13}C NMR ($CDCl_3$) δ: 15.1, 15.1, 24.7, 28.9, 29.5, 30.6, 34.0, 65.5, 66.1, 66.2, 69.4, 69.4, 72.5, 73.3, 122.1, 127.4, 128.3, 129.4, 134.2, 135.3, 155.4, 156.7, 173.3; IR (KBr) ν: 1736 (C=O) cm^{-1}; MS (MALDI-TOF) m/z: 1899.78 $(M + Na)^+$, 1915.73 $(M+K)^+$. Anal. calcd for $C_{112}H_{148}O_{24}$: C 71.62, H 7.94; found C 71.62, H 8.02.

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