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Modular chemistry. Double- and multi-1,3-alternate-calixcrowns

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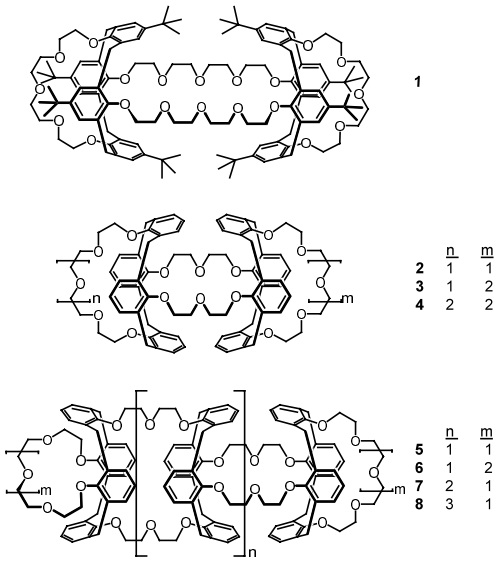
Abstract—Double- and multi-1,3-alternate-calixcrowns were prepared by multistep syntheses.

Because of their easy functionalization calixarenes have been combined in various ways to larger molecules (double- and multi-calixarenes) containing more than one calixarene unit.[1] Due to the special geometry of the calix[4]arene in the 1,3-alternate conformation allowing metal cation tunnelling through the π-basic tube of the calix unit[2] chemists have prepared 'nano-tubes' consisting of two or more calixarene units in the 1,3-alternate conformation. In 1992, Asfari et al.[3] reported the reaction of *p-tert*-butyl calix[4]arene with an excess of tetraethylene glycol ditosylate and K_2CO_3 leading to the double calix[4]biscrown-5 (**1**) in which the two calix[4]crown-5 are crowned constraining the calixarenic units into the 1,3-alternate conformation.[3] Selectivity of complexation was observed for K^+ and Rb^+, the cation being located in the central cavity of the tritopic receptor.[3] Subsequently, Asfari et al.[4] obtained similar structures from a mesitol-derived calix[4]arene known to exist in the 1,3-alternate conformation. More recently, Kim et al.[5] obtained a dimeric structure by reacting 1,3-dipropyl calix[4]arene with *N*-tosyl tetraethylene glycol dimesylate and Cs_2CO_3.[5] The calixarene units were shown to be in the 1,3-alternate conformation.[5] Nano-tubes consisting of two[6–8] or three[6] calix[4]arene units in the 1,3-alternate conformation have also been constructed by linkages at the *para* position instead of the phenolic oxygens.

As part of our work on calix[4]crown compounds[2,9,10] we report in this letter the synthesis of 1,3-calix[4]crown polymers: dimers **2**–**4**, trimers **5** and **6**, tetramer **7** and pentamer **8** in which all the calixcrown units are in the 1,3-alternate conformation and are linked to one another by crown elements giving rise to polytopic receptors with tubular structures.



Synthesis of dimers 2–4. Scheme 1 shows the synthesis of dimers **2**–**4**. 1,3-Calix[4]*mono*crown-5 (**9**)[11] or 1,3-calix[4]*mono*crown-6 (**10**)[11] was reacted with 3 equiv. of diethylene glycol monotosylate in the presence of 2 equiv. of Cs_2CO_3 in refluxing acetonitrile for 24 h under N_2.[12]

Chromatography on a silica column (eluent: ethyl acetate) gave diglycolic 1,3-calix[4]*mono*crowns **11** (90% yield) and **12** (92% yield) in the 1,3-alternate conformation with singlets at 3.83 and 3.77 ppm for the ArCH_2Ar protons in their respective ^{1}H NMR spectra. Tosylation of the hydroxyl groups was carried out with 4 equiv. of tosyl chloride (TsCl) in THF in the presence of 10 equiv. of NaOH dissolved in water. Chromatog-

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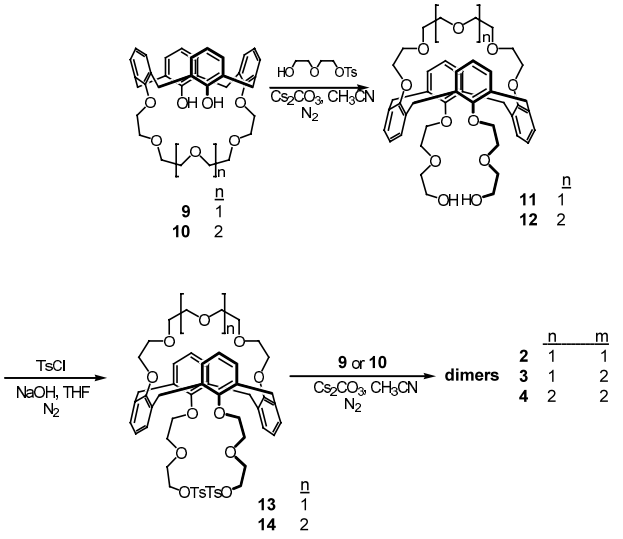
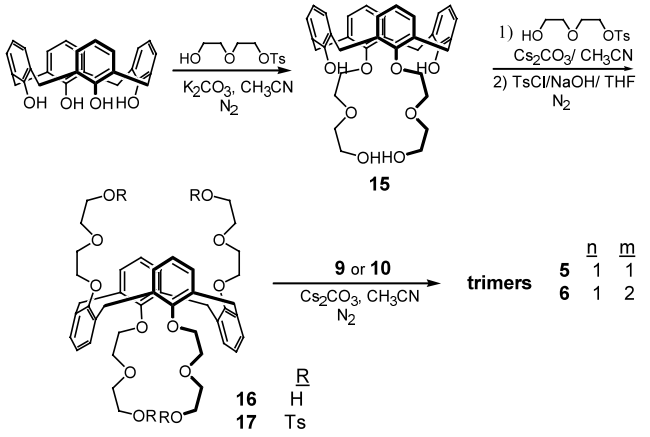


Scheme 1. Synthesis of dimers **2**–**4**.

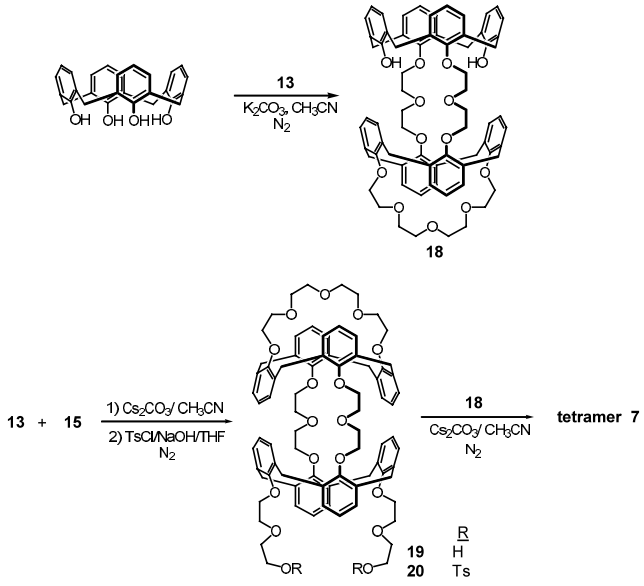
raphy on a silica column using (eluent: ethyl acetate/hexane (3:1)) gave calix ditosylates **13** (80% yield) and **14** (78% yield). ^{1}H NMR showed the 1,3-alternate conformation was maintained during tosylation. Next, **9** was reacted with 1 equiv. of **13** or **14** and 3 equiv. of Cs_2CO_3 in refluxing acetonitrile for 24 h to afford respectively *symmetrical* (the two calix crowns units are the same) dimer **2** (41% yield) by recrystallization from ethyl acetate:chloroform (4:1) and *unsymmetrical* **3** (35% yield) separated by chromatography on a silica column (eluent: ethyl acetate) followed by recrystallisation from diethyl ether:chloroform (4:1). Similarly dimer **4** was obtained in 20% yield by running a similar reaction between **10** and **14**.

Synthesis of trimers 5 and 6. According to Scheme 2, calix[4]arene[13] was reacted with 2 equiv. of diethylene glycol monotosylate in the presence of 1 equiv. of K_2CO_3 in refluxing acetonitrile for 24 h to produce diglycolic calix **15** (44% yield) after recrystallization from CH_2Cl_2/ethyl acetate (1:5). **15** Was reacted once again with diethylene glycol monotosylate but using Cs_2CO_3 to afford tetraglycolic calix **16** which was transformed into its tetratosylate **17** as previously done to obtain **13**. The 1,3-alternate conformation of **16** and **17** was deduced from the presence of singlets at 3.78 and 4.18 ppm for the ArCH_2Ar protons in their respective ^{1}H NMR spectra. Acting as a central unit **17** was reacted with **9** or **10** to afford trimers **5** (25% yield) and **6** (34% yield) after a work up similar to the one of dimers **2**–**4**.

Synthesis of tetramer 7. According to Scheme 3, calix[4]arene[13] was reacted with 1 equiv. of calix ditosylate **13** in the presence of 1 equiv. of K_2CO_3 in refluxing acetonitrile for 24 h to produce double calix **18** (40% yield) after chromatography on silica (eluent: ethyl acetate/hexane (1:1)) and recrystallization from ethyl acetate. The spectrum of **18** showed one AB system with two doublets at 4.40 and 3.52 ppm with $J=12.72$ Hz and one singlet at 3.92 ppm for the ArCH_2Ar



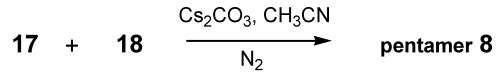
Scheme 2. Synthesis of trimers **5** and **6**.



Scheme 3. Synthesis of tetramer **7**.

protons with a 1:1 integration ratio indicative of both cone and 1,3-alternate conformation. The ^{13}C NMR spectra reflected both conformations with two signals at 38.8 ppm (1,3-alternate) and 32.2 ppm (cone).[14] **20** Was prepared by reacting **13** with 1 equiv. of **15** in the presence of 3 equiv. of Cs_2CO_3 to give **19** (35% yield) which was then tosylated into **20** (78% yield). Double calix **18** was therefore reacted with **20** to produce tetramer **7** (81% yield). The tetrameric structure of **7** was in agreement with the analytical data.

Synthesis of pentamer 8. According to Scheme 4, tetratosylate **17** and double calix **18** were reacted to produce pentamer **8** (31% yield). The analytical data of all the products were in agreement with the proposed structures. The structures of dimers **2**–**4**, trimers **5** and **6**, tetramer **7** and pentamer **5** were deduced from mass spectra. The high symmetry of their molecular structure was reflected in the ^{1}H NMR and ^{13}C NMR spectra which presented very simple patterns.



Scheme 4. Synthesis of pentamer **8**.

Table 1. % Extraction of alkali metal picrates by ligands **2–8**[a]

	% Extraction			
Ligand	Na^+	K^+	Rb^+	Cs^+
2	16.42	**155.76**	**136.91**	54.44
3	14.18	**130.76**	**121.1**	**101.14**
4	17.46	72.75	72.52	**113.31**
5	9.41	**157.72**	**143.78**	38.89
6	1.94	15.03	46.48	89.95
7	5.07	**144.8**	**132.85**	38.01
8	23.58	**122.47**	**116.45**	34.82

[a] Conditions: **2–8**, 0.1 mM in 1,2-dichloroethane; metal picrate, 0.2 mM in water. The intensities of the extracted picrates ($\lambda_{max}=373$ nm) from the water into the organic layer were measured.

Two-phase extraction studies. Table 1 gives extraction data of alkali metal picrates from water to 1,2-dichloroethane by ligands **2–8**. K^+ and Rb^+ were better extracted by **2**, **5**, **7** and **8**. This is probably due to complexation of these cations in the crown-5 loop, the cavity size of which (five oxygen atoms) is known to be appropriate for them as described for 1,3-calix[4]crowns-5.[2]

Similarly, Cs^+ was better extracted by **4** and **6** for similar reasons, since 1,3-calix[4]crowns-6 are known to be suitable for this cation.[2] Ligand **3** which is a hybrid structure containing both crown-5 and crown-6 units was observed to extract the three cations in almost the same percentage range. Concerning Cs^+/Na^+ selectivity the highest one was observed for trimer **6** to be equal to 46.4. The second observation is that as some extraction percentages are higher than 100% (bold numbers), one can assume the formation of binuclear 1:2 ligand:metal complexes.

In this paper we have described the construction of polymers made of 1,3-alternate calix[4]crowns by multi-step procedure. Preliminary extraction studies indicated the formation of 1:2 ligand/metal complexes. The binding properties of polytopic receptors **2–8** are currently under investigation and will be presented in more detail in due course.

Acknowledgements

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12. Melting points (mps) were taken with a Mel-Temp of Fisher–Johns apparatus without any correction. ^1H and ^{13}C NMR spectra were recorded with a 400 MHz (Bruker ARX-600) and a 100 MHz spectrometer, respectively, the chemical shifts (δ) reported in ppm downfield from the internal standard, tetramethylsilane. FAB^+ mass spectra was obtained from JEOL-JMS-HX 110A/110A High Resolution Tandem Mass Spectrometry in Korea Basic Science Institute in Daejon, Korea. All the chemicals were of commercial value and used without any further purification. All the reactions were run under N_2. **Compound 11. 9**[11] (2.00 g; 3.43 mmol), diethyleneglycol monotosylate (2.68 g; 10.3 mmol), Cs_2CO_3 (3.32 g; 10.2 mmol), acetonitrile (100 mL) were refluxed for 24 h. After removing the solvents, the brownish solid residue was dissolved in 5% aqueous HCl (100 mL) and CH_2Cl_2 (50 mL). The organic layer was washed three times with water (50 mL) and dried over anhydrous $MgSO_4$. After filtration and evaporation, the crude residue was chromatographed on silica gel using ethyl acetate as eluent to give **11** as a yellowish oil. Yield: 90%. ^1H NMR (400 MHz, $CDCl_3$): δ 7.15 (d, 4H, Ar-H_m, $J=6.82$ Hz), 7.09 (d, 4H, Ar-H_m, $J=6.80$ Hz), 6.94–6.91 (m, 4H, Ar-H_p), 3.71–3.23 (m, 32H, -OCH_2CH_2O-), 3.83 (s, 8H, Ar-CH_2-Ar), 2.27 (s, 2H, -*OH*). ^{13}C NMR (100 MHz, $CDCl_3$): 156.8, 156.5, 134.7, 134.1, 130.6, 130.5, 124.1, 123.6, 73.4, 71.4, 71.3, 70.5, 70.3, 68.8, 62.1, 38.7, 38.6, 38.5, 31.6. FAB MS m/z (M^+) calcd 758.2, found 758.6. **Compound 12.** Same procedure as for **11**: **10**[11] (3.19 mmol),

diethyleneglycol monotosylate (9.57 mmol), acetonitrile (100 mL), reflux 24 h. Yellowish oil. Yield: 92%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14 (d, 4H, Ar-H_m, $J=7.43$ Hz), 7.10 (d, 4H, Ar-H_m, $J=7.52$ Hz), 6.94–6.86 (m, 4H, Ar-H_p), 3.73–3.46 (m, 36H, -OCH_2CH_2O-, -OH), 3.77 (s, 8H, Ar-CH_2-Ar). ^{13}C NMR (100 MHz, $CDCl_3$): 156.9, 156.7, 134.6, 134.5, 131.0, 130.0, 124.0, 123.9, 73.5, 71.9, 71.8, 71.4, 70.5, 70.3, 62.0, 38.3. FAB MS m/z (M^+) calcd 803.1, found 802.9. **Compound 13.** To a solution of **11** (2.00 g; 2.64 mmol), TsCl (2.01 g; 10.5 mmol) in THF (100 mL) in an ice bath was added dropwise a NaOH solution (0.85 g, 26.4 mmol) in 5 mL of water. After 24 h stirring at rt, the solvents were removed to give a yellowish oil. The crude product was extracted with CH_2Cl_2 (100 mL) and water (100 mL). The organic layer was dried over anhydrous $MgSO_4$. After filtration and evaporation, the crude mixture was chromatographed on silica gel (ethyl acetate/hexane (3:1) as eluent) to give **13** as a colorless oil. Yield: 80%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, 4H, Ar-H-tosyl, $J=7.92$ Hz), 7.34 (d, 4H, Ar-H-tosyl, $J=7.92$ Hz), 7.09 (d, 4H, Ar-H_m, $J=$ 7.45 Hz), 6.99 (d, 4H, Ar-H_m, $J=7.47$ Hz), 6.90 (t, 2H, Ar-H_p, $J=7.45$ Hz), 6.76 (t, 2H, Ar-H_p, $J=7.47$ Hz), 4.09–3.07 (m, 32H, -OCH_2CH_2O-), 3.81 (s, 8H, Ar-CH_2-Ar), 2.43 (s, 6H, Ar-CH_3-tosyl). FAB MS m/z (M^+) calcd 1067.27, found 1066.2. **Compound 14.** Same procedure as for **13**: **12** (2.49 mmol), TsCl (7.47 mmol), NaOH (24.9 mmol) in water (5 mL). Yellowish oil. Yield: 78%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, 4H, Ar-H-tosyl, $J=7.88$ Hz), 7.33 (d, 4H, Ar-H-tosyl, $J=7.88$ Hz), 7.08 (d, 4H, Ar-H_m, $J=7.42$ Hz), 7.01 (d, 4H, Ar-H_m, $J=7.47$ Hz), 6.83 (t, 2H, Ar-H_p, $J=7.42$ Hz), 6.72 (t, 2H, Ar-H_p, $J=7.47$ Hz), 4.13–3.19 (m, 36H, -OCH_2CH_2O-), 3.74 (s, 8H, Ar-CH_2 -Ar), 2.43 (s, 6H, Ar-CH_3-tosyl). ^{13}C NMR (100 MHz, $CDCl_3$): 156.9, 156.5, 145.1, 134.1, 133.4, 130.2, 130.1, 128.3, 122.8, 122.5, 71.5, 71.3, 70.1, 70.0, 69.6, 69.5, 68.9, 37.9. FAB MS m/z (M^+) calcd 1111.32, found 1110.1. **Dimer 2.** Same procedure as for **11**: **9** (0.55 g, 0.94 mmol), **13** (1.00 g, 0.94 mmol), Cs_2CO_3 (0.93 g, 2.85 mmol), acetonitrile (100 mL), reflux 24 h. Brownish solid residue. Recrystallization from ethyl acetate/$CHCl_3$ (4:1) gave **2** as a white solid. Mp 380°C (dec.). Yield: 41%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18 (d, 8H, Ar-H_m, $J=7.40$ Hz), 7.09 (d, 8H, Ar-H_m, $J=7.46$ Hz), 7.03 (t, 4H, Ar-H_p, $J=7.40$ Hz), 6.92 (t, 4H, Ar-H_p, $J=7.46$ Hz), 3.91 (s, 16H, Ar-CH_2-Ar), 3.60–2.54 (m, 48H, -OCH_2CH_2O-). ^{13}C NMR (100 MHz, $CDCl_3$): 156.7, 156.1, 134.3, 129.2, 129.1 129.0, 123.3, 122.6, 73.0, 70.9, 70.1, 69.2, 68.5, 66.4, 38.3. FAB MS m/z (M^+) calcd. 1305.5, found 1305.3. **Dimer 3.** Same procedure as for **11**. **10** (0.94 mmol), **13** (0.94 mmol), Cs_2CO_3 (2.82 mmol), acetonitrile (100 mL), reflux 24 h. Brownish residue. Column chromatography on silica gel using ethyl acetate as an eluent followed by recrystallization from diethyl ether/$CHCl_3$ (4:1) gave **4** as a white solid. Mp 395°C (dec.). Yield: 35%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19 (d, 8H, Ar-H_m, $J=7.38$ Hz), 7.11–7.01 (m, 8H, Ar-H_m; 4H Ar-H_p), 6.95–6.89 (m, 4H, Ar-H_p), 3.90 (s, 16H, Ar-CH_2 -Ar), 3.68–2.54 (m, 52H, -OCH_2CH_2O-); ^{13}C NMR (100 MHz, $CDCl_3$): 156.7, 156.1, 134.3, 129.2, 129.1 129.0, 123.3, 122.6, 73.0, 71.0, 69.9, 69.3, 68.5, 66.3, 38.3. FAB MS m/z (M^+) calcd 1348.6, found 1349.5. **Dimer 4.** Same procedure as for **11**. **10** (1.56 mmol), **14** (1.56 mmol), Cs_2CO_3 (4.68 mmol), acetonitrile (100 mL), reflux 24 h. White solid. Mp 384°C (dec.). Yield: 20%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19 (d, 8H, Ar-H_m, $J=7.43$ Hz), 7.09 (d, 8H, Ar-H_m, $J=7.30$ Hz), 7.03 (t, 4H, Ar-H_p, $J=7.30$ Hz), 6.92 (t, 4H, Ar-H_p, $J=7.43$ Hz), 3.91 (m, 16H, Ar-CH_2–Ar), 3.69–2.57 (m, 52H, -OCH_2CH_2O-). ^{13}C NMR (100 MHz, $CDCl_3$): 157.2, 156.1, 134.3, 129.4, 129.2, 123.3, 122.7, 71.4, 71.0, 69.9, 69.7, 69.3, 66.4, 38.4. FAB MS m/z (M^+) calcd 1392.6, found 1392.6. **Compound 15.** Same procedure as for **11**. Calix[4]arene[13] (3.00 g, 7.07 mmol), diethyleneglycol mono-*p*-toluenesulfonate (3.86 g, 14.8 mmol), K_2CO_3 (0.98 g, 7.07 mmol), acetonitrile (100 mL) were refluxed for 24 h. White solid. Recrystallization from CH_2Cl_2/ethyl acetate (1:5) gave **15** as a white solid. Mp 191–193°C. Yield: 44%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.00 (s, 2H, Ar-OH), 7.05 (d, 4H, Ar-H_m, $J=5.04$ Hz), 7.01 (d, 4H, Ar-H_m, $J=4.52$ Hz), 6.81 (t, 2H, Ar-H_p, $J=5.04$ Hz), 6.66 (t, 2H, Ar-H_p, $J=4.52$ Hz), 4.74 (broad s, 2H, -OH), 4.43 (d, 4H, Ar-CH_2-Ar, $J=13.12$ Hz), 4.17 (broad s, 8H, -OCH_2CH_2O-), 3.81 (broad s, 8H, -OCH_2CH_2O-), 3.40 (d, 4H, Ar-CH_2-Ar, $J=13.12$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$): 152.6, 151.9, 134.7, 131.5, 129.7, 129.1 126.5, 120.6, 76.3, 74.2, 70.3, 62.7, 31.7. FAB MS m/z (M^+) calcd 600.70, found 601.2. **Compound 16.** Same procedure as for **11**. **15** (2.00 g, 3.33 mmol), diethylene-glycol mono-*p*-toluenesulfonate (2.82 g, 6.66 mmol), Cs_2CO_3 (3.25 g, 9.99 mmol), acetonitrile (100 mL), reflux 24 h. White solid. Recrystallization from CH_2Cl_2/ethyl acetate (1:5) gave **12** as a white solid. Mp 198–201°C. Yield: 73%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13 (d, 8H, Ar-H_m, $J=6.69$ Hz), 6.91 (t, 4H, Ar-H_p, $J=6.69$ Hz), 3.82 (s, 8H, Ar-CH_2-Ar), 3.78 (broad s, 4H, -OH), 3.72 (broad s, 16H, -OCH_2CH_2O-), 3.62 (broad s, 16H, -OCH_2CH_2O-). FAB MS m/z (M^+) calcd 776.9, found 777.3. **Compound 17.** Same procedure as for **13**. **16** (2.00 g, 2.52 mmol), TsCl (2.16 g, 11.4 mmol), THF (100 mL), NaOH (1.01 g, 25.2 mmol) dissolved in water (5 mL). Colorless oil. Column chromatography on silica gel using CH_2Cl_2/methanol (19:1) as eluent gave **17** as a colorless oil. Yield: 85%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, 8H, Ar-H-tosyl, $J=7.20$ Hz), 7.32 (d, 8H, Ar-H-tosyl, $J=7.20$ Hz), 6.97 (d, 8H, Ar-H_m, $J=7.14$ Hz), 6.64 (t, 4H, Ar-H_p, $J=7.14$ Hz), 4.18 (s, 8H, Ar-CH_2-Ar), 3.66–3.46 (m, 32H, -OCH_2CH_2O-), 2.42 (s, 12H, Ar-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): 156.5, 145.5, 134.2, 133.7, 130.5, 128.6, 122.7, 71.0, 70.9, 70.0, 69.3, 36.7, 22.3. FAB MS m/z (M^+) calcd 1393.6, found 1393.5. **Trimer 6: 17** (3.00 g, 2.15 mmol), **9** (2.51 g, 4.30 mmol), Cs_2CO_3 (4.21 g, 12.9 mmol), acetonitrile (100 mL) were refluxed for 24 h. After evaporation, the resulting solid was dissolved in $CHCl_3$ (100 mL) and 5% aqueous HCl (100mL). The organic layer was washed three times with water and dried over anhydrous $MgSO_4$. After filtration and evaporation the obtained white solid was recrystallized from $CHCl_3$/ethyl acetate (1:2) to give **6** as a white solid. Mp 348–351°C (dec.). Yield: 25%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18 (dd, 16H, Ar-H_m, $J=38$, $J=7.12$), 7.11–7.00 (m, 8H, Ar-H_m; 8H, Ar-H_p), 6.95 (t, 4H, Ar-H_p, $J=7.75$ Hz), 3.97–3.87 (m, 24H, Ar-CH_2-Ar), 3.59–3.53 (m, 16H, -OCH_2CH_2O-diethyleneglycol spacers; 16H, -OCH_2-CH_2O-crown-5), 3.39 (t, 8H, -OCH_2CH_2O-crown-5, $J=$ 6.13 Hz), 3.07 (t, 8H, - OCH_2CH_2O-crown-5, $J=6.38$

Hz), 2.56–2.53 (m, 16H, -OCH_2CH_2O- diethyleneglycol spacers). ^{13}C NMR (100 MHz, $CDCl_3$): 156.8, 156.3, 156.1, 134.4, 129.1, 128.7, 123.4, 122.7, 73.0, 71.0, 70.2, 69.3, 68.6, 66.5, 38.4. FAB MS m/z (M^+) calcd 1868.9, found 1869.9. **Trimer 7:** Same procedure as for **16**: with the same molar quantities. White solid. Mp 381–392°C (dec.). Yield: 34%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21–7.18 (dd, 16H, Ar-H_m, J=6.09 Hz, J=6.35 Hz), 7.10–7.02 (m, 8H, Ar-H_m; 8H, Ar-H_p), 6.92 (t, 4H, Ar-H_p, J=6.69 Hz), 3.94 (d, 24H, Ar-CH_2-Ar, J=13.24 Hz), 3.68 (s, 8H, -OCH_2CH_2O-crown-6), 3.62–3.54 (m, 16H, -OCH_2CH_2O-diethyleneglycol spacers; 16H, -OCH_2CH_2O-crown-6), 3.38 (t, 8H, -OCH_2CH_2O-crown-6, J=3.79 Hz), 3.23 (t, 8H, -OCH_2CH_2O-crown-6, J=5.84 Hz), 2.59–2.51 (m, 16H, -OCH_2CH_2O- diethyleneglycol spacers). ^{13}C NMR (100 MHz, $CDCl_3$): 157.6, 156.7, 156.5, 134.7, 129.7, 129.1, 123.3,123.0, 71.8, 71.4, 70.3, 70.1, 69.7, 38.8. FAB MS m/z (M^+) calcd 1958.3, found 1958.5. **Compound 18:** Same procedure as for **11**: calix[4]arene (2.00 g, 4.71 mmol), **13** (5.03 g, 4.71 mmol), K_2CO_3 (0.65 g, 4.71 mmol), acetonitrile (100 mL), reflux 24 h. Brownish solid. Column chromatography on silica gel using ethyl acetate/hexane (1:1) as eluent and recrystallization from ethyl acetate gave **18** as a white solid. Mp 321–329°C (dec.). Yield: 40%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (broad s, 2H, Ar-OH), 7.13–6.92 (m, 12H, Ar-H_m; 4H, Ar-H_p), 6.81–6.78 (m, 2H, Ar-H_p), 6.66–6.62 (m, 2H, Ar-H_p), 4.40 (d, 4H, Ar-CH_2-Ar, J=14.31 Hz), 4.18–4.17 (broad t, 4H, -OCH_2CH_2O-), 3.95–3.92 (m, 8H, Ar-CH_2-Ar; 4H, -OCH_2CH_2O-), 3.63–3.41 (m, 4H, Ar-CH_2-Ar; 16H, -OCH_2CH_2O-), 3.17–3.09 (m, 8H, -OCH_2CH_2O-). ^{13}C NMR (100 MHz, $CDCl_3$): 157.1, 156.9, 153.8, 152.3, 134.6, 129.8, 129.1, 126.3, 123.6, 120.0, 75.4, 73.5, 71.4, 70.9, 70.4, 68.9, 68.4, 38.8, 32.2, 30.3. FAB MS m/z (M^+) calcd 1147.4, found 1147.5. **Compound 19:** Same procedure as for **18**: **13** (3.33 mmol), **15** (3.33 mmol), Cs_2CO_3 (9.99 mmol), acetonitrile (100 mL), reflux 24 h. White solid. Mp 358–365°C (dec.). Yield: 35%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22–7.19 (m, 8H, Ar-H_m), 7.11–7.02 (m, 8H, Ar-H_m; 4H, Ar-H_p), 6.93 (t, 4H, Ar-H_p, J=7.60 Hz), 3.93 (broad s, 16H, Ar-CH_2-Ar), 3.65–3.40 (m, 32H, -OCH_2CH_2O-), 3.21 (t, 4H, -OCH_2CH_2O-crown-5, J=4.77 Hz), 3.04 (t, 4H, -OCH_2CH_2O-crown-5, J=6.53 Hz), 2.66–2.57 (m, 8H, -OCH_2CH_2O-diethyleneglycol spacers). FAB MS m/z (M^+) calcd 1323.6, found 1323.9. **Compound 20:** Same procedure as for **13**: **19** (1.51 mmol), TsCl (4.53 mmol), THF (100 mL), NaOH (15.1 mmol) in water (5 mL). Colorless oil. Yield: 78%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82–7.80 (d, 4H, Ar-H-tosyl, J=7.76 Hz), 7.35–7.33 (d, 4H, Ar-H-tosyl, J=7.76 Hz), 7.19–7.17 (m, 8H, Ar-H_m), 7.10 (d, 4H, Ar-H_m, J=7.39 Hz), 7.05–6.99 (m, 4H, Ar-H_m; 4H, Ar-H_p), 6.94 (t, 2H, Ar-H_p, J=7.39 Hz), 6.82 (t, 2H, Ar-H_p, J=7.41 Hz), 4.04 (broad s, 4H, -OCH_2CH_2O-), 3.97–3.82 (m, 16H, Ar-CH_2 –Ar), 3.60–3.03 (m, 36H, -OCH_2CH_2O-), 2.57–2.56 (m, 8H, -OCH_2CH_2O-diethyleneglycol spacers). ^{13}C NMR (100 MHz, $CDCl_3$): 156.8, 156.1, 145.1, 134.3, 133.4, 130.2, 130.1, 129.3, 129.2, 128.9, 128.3, 123.2, 122.9, 122.6, 73.0, 70.9, 70.1, 69.2, 68.8, 66.4, 60.7, 38.6, 38.3, 38.1, 22.2, 21.4. **Tetramer 7: 20** (1.00 g, 0.61 mmol), **18** (0.70 g, 0.61 mmol), Cs_2CO_3 (0.60 g, 1.83 mmol), acetonitrile (100 mL) were refluxed for 24 h. Work-up procedure was the same as for **6**. White solid. Mp 338–345°C (dec.). Yield: 81%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19 (broad s, 12H, Ar-H_m), 7.09–7.03 (m, 20H, Ar-H_m; 4H, Ar-H_p), 6.95–6.91 (m, 12H, Ar-H_p,), 3.95–3.87 (m, 32H, Ar-CH_2-Ar), 3.57–3.54 (m, 24H, -OCH_2CH_2O-diethyleneglycol spacers; 16H, -OCH_2CH_2O-crown-5), 3.39 (broad s, 8H, -OCH_2CH_2O-crown-5), 3.06 (broad s, 8H, -OCH_2CH_2O-crown-5), 2.56–2.50 (m, 24H, -OCH_2CH_2O- diethyleneglycol spacers). ^{13}C NMR (100 MHz, $CDCl_3$): 157.1, 156.6, 156.5, 134.7, 130.1, 129.6, 129.4, 129.1, 123.7, 123.3, 73.4, 71.3, 70.5, 69.6, 68.9, 66.8, 38.7. FAB MS m/z (M^+) calcd 2434.9, found 2433.8. **Pentamer 8: 17** (1.00 g, 0.72 mmol), **18** (1.65 g, 1.44 mmol), Cs_2CO_3 (0.94 g, 2.87 mmol), acetonitrile (100 mL) were refluxed for 24 h. Work-up procedure was same as for **6**. White solid. Mp 369–385°C (dec.).Yield: 37%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18 (broad s, 20H, Ar-H_m), 7.09 (m, 20H, Ar-H_m; 10H, Ar-H_p), 6.93 (m, 10H, Ar-H_p), 3.95 (broad m, 40H, Ar-CH_2-Ar), 3.55 (broad s, 32H, -OCH_2CH_2O-diethyleneglycol spacers; 16H, -OCH_2CH_2O-crown-5), 3.39 (broad s, 8H, -OCH_2CH_2O-crown-5), 3.05 (broad s, 8H, -OCH_2CH_2O-crown-5), 2.53 (broad m, 32H, -OCH_2CH_2O- diethyleneglycol spacers). ^{13}C NMR (100 MHz, $CDCl_3$): 155.6, 133.8, 133.6, 128.8, 123.5, 72.3, 70.3, 69.6, 68.8, 68.2, 40.6, 40.4, 40.2, 40.0,39.8, 39.5, 37.8. FAB MS m/z (M^+) calcd 2999.6, found 2999.1.

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