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Synthesis, characterization and complexation behavior investigations of novel starburst-like tris-crown ethers

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The novel unique structures of starburst-like tris-crown ethers were successfully synthesized from 1,3,5-triacryloylhexahydro-1,3,5-triazine (TAHTA) with amino- and aza- crown ethers through Michael addition. The crown ethers contained primary and secondary amine groups such as 2-aminomethyl crown ethers, 4-aminobenzo crown ethers and 1-aza crown ethers. The newly synthesized starburst tris-crown ethers were characterized by elemental analysis, IR, ^{1}H-NMR, ^{13}C-NMR and FAB mass spectroscopy, respectively. The newly synthesized host compounds of tris-crown ethers showed complexation abilities with various sizes of alkali metal cations such as Na^+, K^+, Rb^+ and Cs^+. The complexation behavior was examined by ^{1}H-NMR, FAB mass spectroscopy and UV spectroscopy.

Introduction

The chemistry of multi-site crown ethers has recently attracted considerable attention because of their fascinating structures, high abilities to complex with guest cations[1–12] and applications in synthetic, medical, host–guest and supramolecular chemistry.[13–20] Recently, the complexation behavior of crown ethers with alkali metals and other cations has been widely investigated. When the metal cation's radius exactly fits the size of the crown ether unit, it always forms a 1 : 1 host/guest complex. However, compounds that consist of more than two crown ether units in the same molecule may produce "sandwich" type complexes with the metal cations. When the size exceeds that of the crown ether cavity, such as in the "butterfly crown ethers",[21–24] it may form a host/guest 2 : 1 sandwich type complex.[21–29]

We have reported an efficient synthetic approach to tris-, tetra- and penta- crown ethers by using Michael addition with multi-acrylates as linking ligands.[17–20] This synthetic route is very effective and simple. The novel host compounds that contain multi-site crown rings are of great interest because they can form 1 : n ($n \geq 3$) host/guest complexes.

In our continuing effort to make new multi-crown ethers, we chose 1,3,5-triacryloylhexahydro-1,3,5-triazine (TAHTA) as the starting material to react with amino- and aza- crown ethers. In addition, these host compounds of tris-crown ethers showed interesting complexation abilities with various sizes of alkali metal cations such as Na^+, K^+, Rb^+ and Cs^+. In this paper we will report the synthesis, characterization and complexation behavior of several new types of tris-crown ether. The new tris-crown ethers lead to original applications for the preparation of new types of host–guest complex. Their properties can be applied in different areas, such as synthetic and medical chemistry, host–guest and supramolecular chemistry.

Results and discussion

TAHTA often plays an important role in polymer fields. In our case, the TAHTA was designed to act as the linker to synthesize novel tris-crown ethers. TAHTA has three active double bonds at the end of each branch chain. The primary and the secondary amine functional groups of 2-aminomethyl crown ethers, 4-aminobenzo crown ethers and 1-aza crown ethers reacted directly with TAHTA in methanol solution at 50 °C. The tris-crown ethers **1** and **2** were prepared through Michael addition of TAHTA with 1-aza-15-crown-5 and 1-aza-18-crown-6. Likewise, **3** and **4** were made from TAHTA with 2-aminomethyl-15-crown-5 and 2-aminomethyl-18-crown-6. Tris-crown ethers **5** and **6** were obtained by a similar synthetic route using the reaction of TAHTA with 4-aminobenzo-15-crown-5 and 4-aminobenzo-18-crown-6. All the reactions took place under mild conditions. The functional groups reacted directly, and we could obtain the products in only one step. The yields were all higher than 70%. The structures of the newly synthesized starburst-like tris-crown ethers are outlined in Fig. 1.

In our previous work,[17,19] we reported that **5** and **6** could also be prepared by reaction of 4-aminobenzo crown ethers with acrylate; but those reactions could be performed in relatively good yields in the presence of catalyst triethylamine and needed a longer time (6 days). This may be ascribed to the fact that the electron rich benzene ring contained in the 4-aminobenzo crown ethers reduced the activity of the amine group.

In the ^{1}H-NMR spectra, the proton signals of **1–6** could be observed at their expected chemical shifts. For example, in the tris-crown ether **1**, the ethereal protons of the crown ether groups appeared as multiplets at 3.58–3.71 ppm. The 1-aza-crown ether CH_2–N–CH_2 proton chemical shift occurred at 2.77 ppm (triplets). The –CO–CH_2–CH_2–N protons which connected the TAHTA with the aza crown ether nitrogen atom appeared at 2.86 ppm as triplets. The TAHTA ring N–CH_2–N protons were observed at 5.3 ppm as a singlet. In the 5.8–6.8 ppm region, the double bond proton signals were not found, indicating that the Michael addition had been accomplished.

The cases of **2–6** were all similar to **1**. The benzene ring proton's chemical shift signals of tris-crown ether **5** and **6** appeared at 6.11–6.20 and 6.74–6.77 ppm, respectively. The –NH proton signals of tris-crown **3** and **5** were not found in their ^{1}H-NMR spectra, and we think that they were mixed-in with the strong intensity peaks of the ethereal protons.

The ^{13}C-NMR spectra revealed the removal of the double bond carbon signals, which were located around the 126 and 130 ppm regions. The C=O carbon chemical shift moved from

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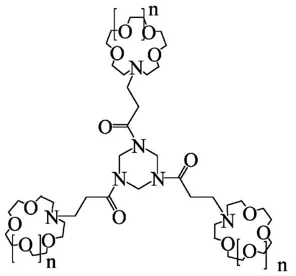
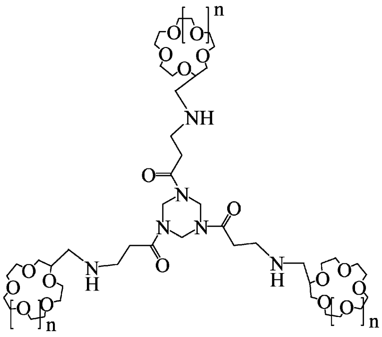
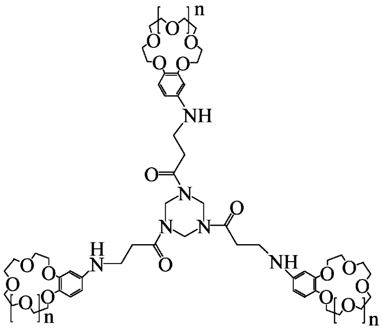


n = 1, starburst tris-crown ether **1**
n = 2, starburst tris-crown ether **2**



n = 1, starburst tris-crown ether **3**
n = 2, starburst tris-crown ether **4**



n = 1, starburst tris-crown ether **5**
n = 2, starburst tris-crown ether **6**

Fig. 1 The structures of the novel starburst-like tris-crown ethers.

165 to 171 ppm. The crown ether carbon chemical shifts were seen around the 69–70 ppm range. The benzene ring carbons of **5** and **6** were found to occur in the range 100–150 ppm. The TAHTA ring N–CH$_2$–N carbons were observed at 56 ppm. All the other carbon atom's chemical shifts of the tris-crown ethers occurred in the positions expected.

Compounds **1–6** were also checked by mass spectrometry. The results further supported the structures of the new tris-crown ethers. The IR spectra revealed that the crown ether C–O–C group absorption peaks occurred around the 1120–1140 cm^{-1} region. In the elemental analyses of **1–6**, we found that all the C, H and N values of the six new tris-crown ethers were within acceptable ranges.

Table 1 Changes in ^{1}H-NMR chemical shifts of the tris-crown ethers **1** and **2** with various metal salts

	Δδ of H-1[a]	Δδ of CH$_2$–N–CH$_2$	Δδ of crown-H	Δδ of TAHTA-H
1 + Na$^+$	−0.024	0.044	−0.013	0.109
1 + K$^+$	−0.044	0.029	−0.015	0.110
1 + Rb$^+$	−0.040	0.017	−0.015	0.089
1 + Cs$^+$	−0.041	0.016	−0.008	0.066
2 + K$^+$	0.018	0.026	−0.112	0.127
2 + Rb$^+$	−0.026	0.024	−0.118	0.098
2 + Cs$^+$	−0.035	0.023	−0.097	0.084

[a] H-1 is the proton of N–CO–CH$_2^2$–CH$_2^1$–N in tris-crown ether **1** and **2**.

Table 2 Changes of ^{1}H-NMR chemical shifts of the tris-crown ethers **3** and **4** with various metal salts

	Δδ of H-3[a]	Δδ of H-4[a]	Δδ of crown-H	Δδ of TAHTA-H
3 + Na$^+$	−0.055	0.161	−0.061	0.059
3 + K$^+$	−0.067	0.147	−0.051	0.037
3 + Rb$^+$	−0.073	0.139	−0.037	0.030
3 + Cs$^+$	−0.072	0.108	−0.043	0.028
4 + K$^+$	0.056	0.105	−0.110	0.084
4 + Rb$^+$	0.052	0.096	−0.083	0.062
4 + Cs$^+$	0.076	0.088	−0.085	0.060

[a] H-3 and H-4 are the protons of N–CO–CH$_2^3$–CH$_2^4$–NH in tris-crown ether **3** and **4**, as indicated in Fig. 2 (A).

The binding interactions of the new host compounds of tris-crown ethers with alkali metal cations were examined by ^{1}H-NMR spectroscopy and by an absorption investigation using UV spectroscopy. The complexes were also checked by using FAB mass spectrometry.

In the ^{1}H-NMR analyses, NaSCN, KSCN, RbSCN and CsSCN were dissolved in acetone-d_6 to make 2 × 10^{-2} M solutions, respectively. **1–4** were dissolved in acetone-d_6 while **5** and **6** were dissolved in chloroform-d to make 5 × 10^{-3} M solutions. Gradual downfield or upfield shifts were observed with increasing concentration of the alkali metal thiocyanate salt in the tris-crown solution. The stoichiometry of the complexation between the tris-crown ether and the alkali metal cation was confirmed to be 1 : 3. For example, with the addition of NaSCN to the tris-crown ether **1** solution, the chemical shift of H-1 (N–CO–CH$_2^2$–CH$_2^1$–N) shifted upfield from 2.704 ppm (chemical shift was relative to acetone-d_6, 2.050 ppm in tris-crown **1–4**) to 2.680 ppm, Δδ = −0.024 ppm. The chemical shift of the aza-crown unit CH$_2$–N–CH$_2$ protons shifted downfield from 2.814 to 2.858 ppm, Δδ = 0.044 ppm. The crown ether ring proton multiple peaks became sharper and their chemical shift range changed from 3.549–3.784 to 3.567–3.786 ppm; the change in crown ring proton peak width, Δδ, being −0.013 ppm with an increased peak intensity. The chemical shift change was due to the interaction of the crown ether rings with the metal cations, indicating that a new complex had formed. The chemical shift of the TAHTA protons shifted from 5.379 to 5.488 ppm (Δδ = 0.109 ppm), meaning that we think the interaction between the TAHTA (N–CO) group and the metal cations had taken place.

The cases of tris-crown ethers **1** and **2** interacting with K$^+$, Rb$^+$ and Cs$^+$ were similar to the above. The changes of ^{1}H-NMR chemical shifts, Δδ, of H-1, aza-crown unit CH$_2$–N–CH$_2$, the changed crown ring proton peak width and the TAHTA chemical shift are summarized in Table 1.

In the cases of tris-crown ethers **3** and **4**, the changes of ^{1}H-NMR chemical shifts, Δδ, of H-3, H-4, the changed crown ring proton peak width and the TAHTA chemical shift are summarized in Table 2.

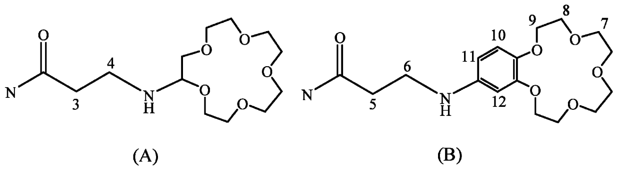


Fig. 2 The proton numbering scheme indicated for the tris-crown compounds **3–6**.

Table 3 Changes of ^{1}H-NMR chemical shifts of the tris-crown ethers **5** and **6** with various metal salts[a]

	$\Delta\delta$ of H-5	$\Delta\delta$ of H-6	$\Delta\delta$ of H-7	$\Delta\delta$ of H-8	$\Delta\delta$ of H-9	$\Delta\delta$ of H-10	$\Delta\delta$ of H-11	$\Delta\delta$ of H-12	$\Delta\delta$ of TAHTA-H
5 + Na^+	0.125	−0.029	0.056	0.050	0.145	0.109	0.226	−0.112	0.153
5 + K^+	0.118	−0.062	0.016	−0.024	−0.093	−0.111	−0.075	−0.152	0.267
5 + Rb^+	0.110	−0.061	−0.007	−0.032	−0.104	−0.096	−0.063	−-0.093	0.265
5 + Cs^+	0.115	−0.049	−0.034	−0.109	−0.096	−0.043	−0.052	−0.087	0.250
6 + K^+	0.143	−0.026	−0.018	0.046	0.171	0.194	0.100	0.043	0.148
6 + Rb^+	0.116	−0.025	−0.024	0.022	0.157	0.180	0.063	0.061	0.146
6 + Cs^+	0.101	−0.037	−0.025	0.017	0.140	0.184	0.076	0.097	0.110

[a] H-5 to H-12 are the protons of in tris-crown ether **5** and **6** as indicated in Fig. 2 (B). The chemical shifts, δ, are relative to tetramethylsilane (TMS) at 0 ppm.

Table 4 The order of increasing absorption of the tris-crown ethers **1–6** under interaction with alkali metal picrate salts in MeOH solution

Tris-crown ether	Order of increasing absorption of the cations
1	$Na^+ < K^+ < Cs^+$
2	$K^+ < Cs^+$
3	$Na^+ < K^+ < Cs^+$
4	$K^+ < Cs^+$
5	$Na^+ < K^+ \approx Cs^+$
6	$K^+ < Cs^+$

The changes of ^{1}H-NMR chemical shifts, $\Delta\delta$, of tris-crown ethers **5** and **6** are shown in Table 3.

In the absorption investigation by UV spectroscopy, the new tris-crown ethers were made into 2×10^{-3} M solutions in methanol. Sodium, potassium and cesium picrate were dissolved in methanol to make very low concentration solutions, respectively. The absorption maximum of the picrate anion in methanol was observed at 354 nm. Interestingly, with the addition of the tris-crown ether solution into the alkali picrate salt solutions, the absorption intensities at 354 nm all increased. The orders of increasing absorption intensity ratio were different however. In the tris-crown ether **1** case, the increasing intensity ratio was $Na^+ < K^+ < Cs^+$. All the orders of increasing intensity are outlined in Table 4. The results indicate that interactions of the new host tris-crown ethers with the guest alkali metal cations of Na^+, K^+ and Cs^+ have taken place in the methanol solution.

Table 5 The FAB mass spectroscopy data of the complexes and the corresponding ion peaks

Complex	Ion peaks (m/z) and their corresponding fragment
1 + NaSCN	930 [**1** + Na^+]; 1011 [**1** + NaSCN + Na^+]; 1091 [**1** + 2NaSCN + Na^+]
1 + KSCN	946 [**1** + K^+]
1 + RbSCN	992 [**1** + Rb^+]
1 + CsSCN	1040 [**1** + Cs^+]
2 + KSCN	1078 [**2** + K^+]; 1175 [**2** + KSCN + K^+]; 1272 [**2** + 2KSCN + K^+]
2 + RbSCN	992 [**2** + Rb^+]
2 + CsSCN	1040 [**2** + Cs^+]
3 + NaSCN	1020 [**3** + Na^+]; 1101 [**3** + NaSCN + Na^+]; 1183 [**3** + 2NaSCN + Na^+]
3 + KSCN	1036 [**3** + K^+]
3 + RbSCN	1082 [**3** + Rb^+]
3 + CsSCN	1130 [**3** + Cs^+]
4 + KSCN	1168 [**4** + K^+]; 1265 [**4** + KSCN + K^+]; 1362 [**4** + 2KSCN + K^+]
4 + RbSCN	1215 [**4** + Rb^+]
4 + CsSCN	1262 [**4** + Cs^+]
5 + NaSCN	1122 [**5** + Na^+]; 1203 [**5** + NaSCN + Na^+]; 1283 [**5** + 2NaSCN + Na^+]
5 + KSCN	1139 [**5** + K^+]
5 + RbSCN	1185 [**5** + Rb^+]
5 + CsSCN	1231 [**5** + Cs^+]
6 + KSCN	1270 [**6** + K^+]; 1368 [**6** + KSCN + K^+]; 1464 [**6** + 2KSCN + K^+]
6 + RbSCN	1316 [**6** + Rb^+]
6 + CsSCN	1364 [**6** + Cs^+]

We attempted to make crystals of the new host/guest complexes but unfortunately did not succeed. However, we used their FAB mass spectra to check for the formation of host/guest complexes. It was observed that there were three peaks appearing after the new host tris-crown ethers were added with guest alkali metal cations that exactly fitted the size of their cavity. For example, after tris-crown ether **1** was added with NaSCN, we observed an ion peak at m/z = 930, which corresponds to the fragmentation product [**1** + Na^+]. The second peak at m/z = 1011 corresponds to [**1** + NaSCN + Na^+]. The third peak at m/z = 1091 is [**1** + 2NaSCN + Na^+]. This indicated that a new complex had formed. When the tris-crown ethers of **3** or **5** were added to NaSCN or the tris-crown ethers **2**, **4** or **6** were added to KSCN (which were the ideal sizes for the respective crown ether cavities) the FAB mass spectra all showed three peaks. Only one peak appeared when the tris-crown ethers complexed with cations that exceeded the size of their cavities. This was due to the formation of intramolecular sandwich type complexes between the larger-sized guest cations and the tris-crown ethers. The FAB mass spectrum data of the complexes are summarized in Table 5. All the results of the mass spectroscopy study were correct and as we had expected.

Depending upon the results described above, we think the newly synthesized tris-crown ethers can capture the metal cations Na^+ and K^+, which are ideally sized for the crown ether rings of 15-crown-5 and 18-crown-6, respectively, forming host/guest 1 : 3 complexes. It is notable that these tris-crown ethers can also complex with larger-sized metal cations such as Rb^+ and Cs^+ to form a sandwich type complex.

Conclusion

In this paper, we have demonstrated that the Michael addition reaction of 1-aza crown with TAHTA produces several novel tri-crown ethers. We found that these reactions could take place directly without protection–deprotection under gentle conditions and in good yields. These complexes may be viewed as having a starburst structure. In addition, we have investigated the interaction between the tris-crown ethers and alkali metal cations. The results indicate that the new tris-crown ethers can capture not only ideally-sized metal cations, but also cations larger than their cavity size to form sandwich type complexes.

Experimental

General procedures and materials

Elemental analyses (C, H, N) were performed using a Vario EL Elementar instrument. The ^{1}H- and ^{13}C-NMR spectra were obtained on a Varian Mercury 300 NMR spectrometer in

$CDCl_3$. Chemical shifts were expressed in ppm using TMS as an internal standard. FAB MS data were obtained from a Jeol JMS 700 mass spectrometer. FT-IR spectra were recorded on a Mattson Instrument Genesis II spectrometer.

All the crown ethers and reagents were purchased from Aldrich and used as received. The solvents were analytical grade, purchased from DC Chemical Co. Ltd. of Korea and used without further purification.

Synthesis of tris-crown ether 1–6

Tris-crown ether 1. TAHTA (25 mg, 0.1 mmol) and 1-aza-15-crown-5 (88 mg, 0.4 mmol) were dissolved in MeOH (5 ml). The mixture was stirred for 24 h at 50 °C. After the solvent was evaporated *in vacuo*, the crude product was purified *via* column chromatography on silica gel (EtOAc), affording 77 mg to tris-crown ether **1** as a yellow oil. Yield 84.9%. ^{1}H-NMR (300 MHz, $CDCl_3$, ppm): 2.66 (t, $J = 6.6$ Hz, 6 H), 2.75 (t, $J = 5.7$ Hz, 12 H), 2.86 (t, $J = 6.9$ Hz, 6 H), 3.59–3.71 (m, 48 H) and 5.30 (s, 6 H); ^{13}C-NMR (75 MHz, $CDCl_3$, ppm): 171.48, 70.86, 70.33, 70.27, 70.08, 69.99, 69.95, 69.84, 69.80, 56.24, 54.48, 52.27 and 31.06; IR (NaCl, cm^{-1}): 2856.3, 1944.2, 1717.6, 1660.7, 1442.6, 1410.3, 1356.1, 1291.9, 1221.8, 1188.7, 1139.5, 948.9, 946.3, 838.4 and 727.2; MS (FAB): $m/z = 907.9$ [M + H]$^+$, calc. for $C_{42}H_{78}N_6O_{15}$, M, 906.6. Anal. calc. for $C_{42}H_{78}N_6O_{15}$: C, 55.61; H, 8.67; N, 9.26. Found: C, 55.43; H, 8.71; N, 9.22%.

Tris-crown ether 2. TAHTA (25 mg, 0.1 mmol) and 1-aza-18-crown-6 (105 mg, 0.4 mmol) were dissolved in MeOH (5 ml) and handled in the same way as **1** to afford 89 mg of tris-crown ether **2** as a yellow oil. Yield 85.7%. ^{1}H-NMR (300 MHz, $CDCl_3$, ppm): 2.67 (t, $J = 6.9$ Hz, 6 H), 2.77 (t, $J = 5.7$ Hz, 12 H), 2.86 (t, $J = 6.9$ Hz, 6 H), 3.58–3.70 (m, 60 H) and 5.31 (s, 6 H); ^{13}C-NMR (75 MHz, $CDCl_3$, ppm): 171.50, 70.74, 70.55, 70.35, 70.27, 70.19, 69.78, 69.62, 56.19, 53.95, 51.32 and 30.91; IR (NaCl, cm^{-1}): 2854.6, 1942.4, 1716.8, 1661.4, 1452.9, 1413.3, 1350.7, 1287.9, 1222.5, 1186.6, 1119.5, 989.3, 945.1, 842.4 and 728.1; MS (FAB): $m/z = 1039.8$ [M + H]$^+$, calc. for $C_{48}H_{90}N_6O_{18}$, M, 1038.6. Anal. calc. for $C_{48}H_{90}N_6O_{18}$: C, 55.47; H, 8.73; N, 8.09. Found: C, 55.22; H, 8.71; N, 8.07%.

Tris-crown ether 3. TAHTA (25 mg, 0.1 mmol) and 2-aminomethyl-15-crown-5 (125 mg, 0.5 mmol) were dissolved in MeOH (5 ml) and handled in the same way as **1** to afford 72 mg of tris-crown ether **3** as a pale yellow oil. Yield 72.2%. ^{1}H-NMR (300 MHz, $CDCl_3$, ppm): 2.53 (t, $J = 6.6$ Hz, 6 H), 2.72 (d, $J = 6.0$ Hz, 6 H), 2.90 (t, $J = 8.4$ Hz, 6 H), 3.61–3.80 (m, 57 H) and 5.29 (s, 6 H); ^{13}C-NMR (75 MHz, $CDCl_3$, ppm): 171.49, 78.24, 72.79, 72.61, 72.28, 70.69, 70.55, 70.39, 70.01, 69.55, 69.39, 68.98, 55.76, 50.82, 44.95 and 33.03; IR (NaCl, cm^{-1}): 3353.4, 2901.5, 2874.3, 1652.8, 1437.1, 1350.2, 1295.7, 1244.3, 1185.6, 1120.2, 1038.4, 987.2, 949.2 and 844.2; MS (FAB) $m/z = 997.7$ [M + H]$^+$, calc. for $C_{45}H_{84}N_6O_{18}$, M, 996.6. Anal. calc. for $C_{45}H_{84}N_6O_{18}$: C, 54.20; H, 8.49; N, 8.43. Found: C, 53.92; H, 8.33; N, 8.28%.

Tris-crown ether 4. TAHTA (25 mg, 0.1 mmol) and 2-aminomethyl-18-crown-6 (147 mg, 0.5 mmol) were dissolved in MeOH (5 ml) and handled in the same way as **1** to afford 81 mg of tris-crown ether **4** as a pale yellow oil. Yield 71.8%. ^{1}H-NMR (300 MHz, $CDCl_3$, ppm): 2.51 (t, $J = 6.6$ Hz, 6 H), 2.70 (d, $J = 6.0$ Hz, 6 H), 2.87 (t, $J = 8.4$ Hz, 6 H), 3.61–3.88 (m, 69 H) and 5.26 (s, 6 H); ^{13}C-NMR (75 MHz, $CDCl_3$, ppm): 171.16, 78.28, 72.88, 72.46, 72.07, 71.51, 70.96, 70.88, 70.79, 70.57, 70.47, 70.40, 70.23, 70.13, 70.05, 69.92, 69.72, 69.55, 69.37, 68.87, 55.87, 50.94, 45.08 and 32.67; IR (NaCl, cm^{-1}): 3351.6, 2902.1, 2870.2, 1655.4, 1435.6, 1351.6, 1293.4, 1242.5, 1181.1, 1122.9, 1041.8, 989.5, 948.2 and 843.8; MS (FAB) $m/z = 1129.8$ [M + H]$^+$, calc. for $C_{51}H_{96}N_6O_{21}$, M, 1128.7. Anal. calc. for $C_{51}H_{96}N_6O_{21}$: C, 54.24; H, 8.57; N, 7.44. Found: C, 54.07; H, 8.49; N, 7.52%.

Tris-crown ether 5. TAHTA (25 mg, 0.1 mmol) and 4-aminobenzo-15-crown-5 (142 mg, 0.5 mmol) were dissolved in MeOH (8 ml). The reaction was begun by adding some triethylamine as catalyst and allowed to continue for 6 d at 50 °C. After this time, the reaction was handled in the same way as **1** to afford 84 mg of tris-crown ether **5** as a red-brown oil. Yield 76.5%. ^{1}H-NMR (300 MHz, $CDCl_3$, ppm): 2.79 (t, $J = 5.4$ Hz, 6 H), 3.39 (t, $J = 5.7$ Hz, 6 H), 3.74–3.77 (m, 24 H), 3.85–3.88 (m, 12 H), 4.03–4.09 (m, 12 H), 5.23 (s, 6 H), 6.11–6.20 (dd, 6 H) and 6.74–6.77 (d, 3 H); ^{13}C-NMR (75 MHz, $CDCl_3$, ppm): 171.18, 150.51, 143.27, 141.22, 117.31, 104.72, 100.80, 70.78, 70.68, 70.61, 70.29, 69.84, 69.49, 55.89, 39.90 and 32.03; IR (NaCl, cm^{-1}): 3364.2, 3031.4, 2904.5, 2861.5, 1642.0, 1606.1, 1505.9, 1452.0, 1418.8, 1357.6, 1216.5, 1184.1, 1128.3, 1057.8, 989.5, 937.2 and 843.3; MS (FAB) $m/z = 1099.7$ [M + H]$^+$, calc. for $C_{54}H_{78}N_6O_{18}$, M, 1098.5. Anal. calc. for $C_{54}H_{78}N_6O_{18}$: C, 59.00; H, 7.15; N, 7.65. Found: C, 59.24; H, 7.12; N, 7.73%.

Tris-crown ether 6. TAHTA (25 mg, 0.1 mmol) and 4-aminobenzo-18-crown-6 (163 mg, 0.5 mmol) were dissolved in MeOH (8 ml) and handled in the same way as **5** to afford **6** as a deep brown oil (94 mg). Yield 76.4%. ^{1}H-NMR (300 MHz, $CDCl_3$, ppm): 2.77 (t, $J = 5.4$ Hz, 6 H), 3.38 (t, $J = 5.7$ Hz, 6 H), 3.67–3.78 (m, 36 H), 3.85–3.90 (m, 12 H), 4.05–4.10 (m, 12 H), 5.23 (s, 6 H), 6.11–6.21 (dd, 6 H) and 6.74–6.77 (d, 3 H); ^{13}C-NMR (75 MHz, $CDCl_3$, ppm): 171.20, 150.09, 143.17, 140.97, 116.60, 104.68, 100.85, 70.56, 69.95, 69.79, 69.55, 68.46, 55.90, 39.94 and 32.03; IR (NaCl, cm^{-1}): 3353.7, 3030.7, 2900.1, 2871.2, 1646.3, 1612.4, 1506.3, 1451.1, 1417.9, 1355.2, 1214.8, 1183.0, 1120.3, 1058.3, 987.7, 940.2 and 842.5; MS (FAB) $m/z = 1231.6$ [M + H]$^+$, calc. for $C_{60}H_{90}N_6O_{21}$, M, 1230.6. Anal. calc. for $C_{60}H_{90}N_6O_{21}$: C, 58.52; H, 7.37; N, 6.82. Found: C, 58.79; H, 7.30; N, 6.73%.

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