

Synthesis and Complexation Behavior Studies of Novel Bis-crown Ethers

ZHI BIN HUANG and SEUNG HYUN CHANG*

Department of Chemistry, Daegu University, 712-714, Kyongbuk, Korea

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Abstract

The novel unique structures of bis-crown ethers were successfully synthesized from tri (propylene glycol) di-acrylate with amino- and aza-crown ethers through Michael addition. The crown ethers contained the primary and the secondary amine group such as 2-aminomethyl crown ethers, 4-aminobenzo crown ethers and 1-aza crown ethers. The newly synthesized bis-crown ethers were characterized by elemental analyses, IR, ^1H NMR, ^{13}C NMR, mass spectrum, respectively. The newly synthesized host compounds of bis-crown ethers showed complex ability with various sizes of alkali metal cations such as Na^+ , K^+ , Rb^+ and Cs^+ . The complexation behavior was examined by ^1H NMR spectroscopy and UV spectrometry.

Introduction

During the past few years significant advances have occurred in the development of host–guest chemistry since the crown ethers were first introduced by Pedersen in 1967 [1]. The chemistry of bis-crown ethers has attracted considerable attentions during the last two decades because of both their fascinate structures and high abilities in complex with guest cations. A wide variety of bis-crown ethers have been synthesized and reported [2–29]. The construction of the molecular receptor molecules capable of binding two or more guest metal cations is one current area of interest in this field [30–38].

Crown ether moiety is one of the most popular host compounds in host–guest chemistry field. And they showed remarkable ability to form strong complexes with alkali metal, alkaline metal and organic cations [39–40]. When the metal cations radii exactly fit the size of the crown ether unit, it always forms a 1:1 host/guest complex. However, compounds that consist of more than one crown ether units in the same molecule, it may produce “sandwich type” complexes with the metal cations. When the cation size exceeds that of the crown ether cavity such as the “butterfly crown ethers” [2–4], it may form a host/guest 2:1 sandwich type complex [41–44].

We have reported the efficient synthetic approach to tris-, tetra- and penta-crown ether by Michael addition using multi-acrylates as linking ligands [35–38]. This synthetic route is very effective and simple. The novel

host compounds that containing multi-site crown rings are of great interesting, they can form 1: n ($n \geq 3$) host/guest complexes.

Tri (propylene glycol) di-acrylate (TPGDA) has the advantage of low viscosity and high solubility in common organic solvents. As our continuing effort to make new bis-crown ethers, it would be a useful attempt to link the crown ethers with di-acrylate of TPGDA and get new structures of bis-crown ethers, which are highly promising solvent-extraction reagents and good host compounds in host–guest chemistry area.

The structure of the novel bis-crown ethers are shown in Figure 1. In addition, these host compounds of bis-crown ethers showed interesting complexation ability with various size of alkali metal cations such as Na^+ , K^+ , Rb^+ and Cs^+ . In this paper, we will report the synthesis, characterization and complexation behavior of a new type of bis-crown ethers. The new bis-crown ethers lead to original applications for the preparation of new types of host–guest complexes. The properties can be applied in various areas, such as synthetic and medical chemistry, host–guest and supramolecular chemistry.

Experimental

General methods

Elemental analyses (C, H, N) were performed using a Vario EL Elementar. The ^1H - and ^{13}C -NMR spectra

* Author for correspondence. E-mail: shchang@daegu.ac.kr

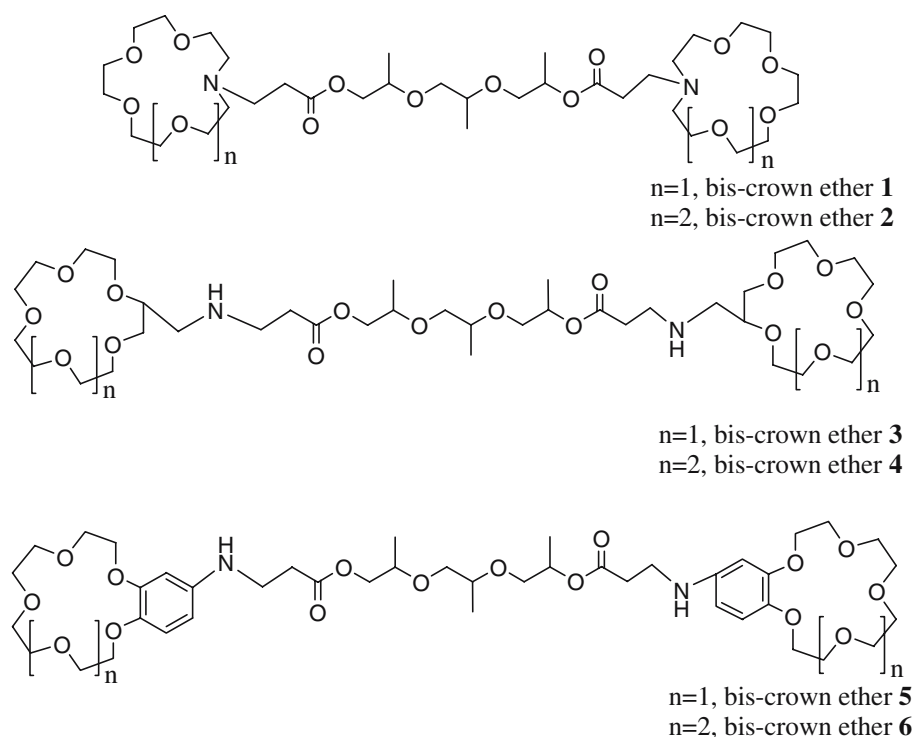


Figure 1. The structures of new bis-crown ethers.

were obtained on a Varian Mercury 300 NMR spectrometer in CDCl_3 . The chemical shifts were expressed in ppm (δ scale) using tetramethylsilane as an internal standard. GC-MS data were obtained from Shimadzu GC-Mass Spectrometer GCMSD-QP5050. FAB MS data were obtained from a Jeol JMS 700 Mass Spectrometer at the Korea Basic Science Institute (Daegu, Korea). FT-IR spectra were recorded on a Mattson Instrument Genesis II spectrometer. The absorption spectrum was taken on Hewlett Packard UV-visible spectrophotometer UV-8453.

Material

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

Synthesis of bis-crown ether (1). TPGDA (60 mg, 0.2 mmol) and 1-aza-15-crown-5 (110 mg, 0.5 mmol) were dissolved in MeOH (5 ml), the reaction was stirred at 50 °C, after 24 h, the solvent was evaporated in vacuo and purified via column chromatography on silica gel (EtOAc), affording 120 mg bis-crown **1** as a yellow oil. Yield 81.3%. ^1H NMR (300 MHz, CDCl_3 , ppm) δ : 1.10–1.24 (m, 9H), 2.48 (t, $J=7.2$ Hz, 4H), 2.76 (t, $J=6.0$ Hz, 8H), 2.88 (t, $J=6.9$ Hz, 4H), 3.27–3.55 (m, 9H), 3.57–3.82 (m, 32H); ^{13}C NMR (75 MHz, CDCl_3 , ppm) δ : 173.11, 75.96, 75.68, 74.66, 73.87, 71.55, 70.95, 70.38, 70.14, 69.93, 69.71, 67.93, 67.04, 66.86, 66.16, 65.75, 54.40, 54.32, 51.96, 51.56, 32.77, 32.52, 18.80, 18.57, 17.89,

17.06, 16.59, 15.93; IR (NaCl, cm^{-1}): 2967.9, 2873.4, 1729.8, 1654.6, 1581.4, 1454.1, 1374.0, 1354.8, 1295.9, 1252.5, 1193.7, 1117.6, 941.1, 836.9; MS(EI): m/z 738.3 $[\text{M}]^+$; Anal. calc. for $\text{C}_{35}\text{H}_{66}\text{N}_2\text{O}_{14}$: C, 56.91; H, 8.94; N, 5.69. Found: C, 56.61; H, 9.09; N, 5.57.

Synthesis of bis-crown ether (2). TPGDA (60 mg, 0.2 mmol) and 1-aza-18-crown-6 (132 mg, 0.5 mmol) were dissolved in MeOH (5 ml), same as above to get 137 mg **2** as yellow oil. Yield 82.9%. ^1H NMR (300 MHz, CDCl_3 , ppm) δ : 1.11–1.25 (m, 9H), 2.48 (t, $J=7.2$ Hz, 4H), 2.76 (t, $J=6.0$ Hz, 8H), 2.89 (t, $J=6.9$ Hz, 4H), 3.25–3.53 (m, 9H), 3.58–3.97 (m, 40H); ^{13}C NMR (75 MHz, CDCl_3 , ppm) δ : 173.20, 75.89, 75.19, 74.91, 74.43, 70.85, 70.72, 70.38, 69.83, 67.09, 66.84, 66.50, 66.23, 65.76, 53.87, 51.56, 51.03, 32.45, 18.59, 18.51, 17.90, 16.89, 16.46; IR (NaCl, cm^{-1}): 2969.8, 2877.3, 1731.7, 1643.1, 1582.3, 1455.0, 1374.0, 1353.8, 1296.9, 1249.6, 1110.8, 1013.4, 987.4, 953.6, 835.0; MS(EI): m/z 826.4 $[\text{M}]^+$; Anal. calc. for $\text{C}_{39}\text{H}_{74}\text{N}_2\text{O}_{16}$: C, 56.66; H, 8.96; N, 3.39. Found: C, 56.92; H, 9.06; N 3.54.

Synthesis of bis-crown ether (3). TPGDA (60 mg, 0.2 mmol) and 2-aminomethyl-15-crown-5 (150 mg, 0.6 mmol) were dissolved in MeOH (5 ml), same as above, obtained 118 mg **3** as slight yellow oil. Yield 73.8%. ^1H NMR (300 MHz, CDCl_3 , ppm) δ : 1.10–1.22 (m, 9H), 2.50 (t, $J=6.6$ Hz, 4H), 2.69 (d, $J=6.0$ Hz, 4H), 2.89 (t, $J=6.9$ Hz, 4H), 3.35–3.55 (m, 9H), 3.56–3.85 (m, 38H); ^{13}C NMR (75 MHz, CDCl_3 , ppm) δ : 173.10, 78.74, 75.99, 74.91, 74.48, 74.06, 72.69, 72.33, 71.98, 71.62, 71.05, 70.96, 70.68, 70.53, 70.43, 70.28, 69.98, 67.18, 66.89, 66.26, 66.11, 65.74, 65.65, 51.58, 51.51, 45.12, 34.57, 18.78, 18.35, 18.06, 17.27, 16.79, 16.41, 15.91; IR (NaCl, cm^{-1}): 2967.0, 2916.8, 2876.3, 1968.0,

1732.7, 1587.1, 1457.0, 1377.9, 1353.8, 1294.5, 1250.6, 1193.7, 1114.7, 984.5, 948.8, 869.7, 833.1; MS(EI): m/z 797.7[M]⁺; Anal. calc. for C₃₇H₇₀N₂O₁₆: C, 55.64; H, 8.77; N, 3.51. Found: C, 55.87; H, 8.86; N, 3.74.

Synthesis of bis-crown ether (4). TPGDA (60 mg, 0.2 mmol) and 2-aminomethyl-18-crown-6 (176 mg, 0.6 mmol) were dissolved in MeOH (5 ml), same as above, gave 133 mg **4** as slight yellow oil. Yield 75.1%. ¹H NMR (300 MHz, CDCl₃, ppm) δ: 1.10–1.24 (m, 9H), 2.52 (t, $J=6.9$ Hz, 4H), 2.70 (d, $J=5.7$ Hz, 4H), 2.89 (t, $J=6.6$ Hz, 4H), 3.35–3.55 (m, 9H), 3.56–3.86 (m, 46H); ¹³C NMR (75 MHz, CDCl₃, ppm) δ: 173.02, 78.67, 75.91, 75.14, 74.38, 70.85, 70.78, 70.72, 70.69, 70.60, 69.65, 67.11, 66.52, 65.91, 51.53, 45.15, 32.59, 18.58, 18.29, 17.90, 16.60; IR (NaCl, cm⁻¹): 2969.8, 2875.4, 1975.7, 1735.6, 1645.9, 1454.1, 1374.0, 1352.8, 1289.2, 1251.6, 1107.9, 988.3, 839.8; MS(EI): m/z 886.2[M]⁺; Anal. calc. for C₄₁H₇₈N₂O₁₈: C, 55.53; H, 8.80; N, 3.16. Found: C, 55.31; H, 9.04; N 3.37.

Synthesis of bis-crown ether (5). TPGDA (60 mg, 0.2 mmol) and 4-aminobenzo-15-crown-5 (170 mg, 0.6 mmol) were dissolved in MeOH (8 ml), the reaction was proceeded by adding some triethylamine as catalyst and continued reacting for 6 days at 50 °C, after the reactions accomplished, operated as above to get 126 mg **5** as red brown oil. Yield 72.7%. ¹H NMR (300 MHz, CDCl₃, ppm) δ: 1.09–1.22 (m, 9H), 2.60 (t, $J=6.3$ Hz, 4H), 3.26–3.54 (m, 13H), 3.66–3.74 (m, 8H), 3.76–3.91 (m, 4H), 4.04–4.10 (m, 4H), 6.18–6.26 (dd, 4H), 6.71–6.79 (d, 2H); ¹³C NMR (CDCl₃, 75 MHz, ppm) δ: 172.92, 150.60, 143.19, 141.41, 117.42, 104.72, 100.95, 75.87, 75.06, 74.29, 73.86, 70.86, 70.67, 70.35, 69.88, 69.52, 68.59, 68.44, 67.06, 66.39, 65.68, 51.76, 33.65, 18.74, 18.30, 17.91, 16.95, 16.66; IR (NaCl, cm⁻¹): 3422.1, 3360.4, 3236.0, 3036.4, 2929.4, 2871.5, 1966.1, 1722.1, 1615.1, 1512.9, 1455.0, 1407.8, 1375.0, 1357.6, 1293.0, 1228.4, 1194.7, 1132.0, 1063.6, 984.5, 937.2, 845.6, 810.9; MS(EI): m/z 866.4[M]⁺; Anal. calc. for C₄₃H₆₆N₂O₁₄: C, 59.58; H, 7.62; N, 3.23. Found: C, 59.37; H, 7.55; N, 3.45.

Synthesis of bis-crown ether (6). TPGDA (60 mg, 0.2 mmol) and 4-aminobenzo-18-crown-6 (196 mg, 0.6 mmol) were dissolved in MeOH (8 ml), operated as above to get 136 mg **6** as deep purple oil. Yield 71.2%. ¹H NMR (300 MHz, CDCl₃, ppm) δ: 1.10–1.24 (m, 9H), 2.61 (t, $J=6.3$ Hz, 4H), 3.27–3.54 (m, 13H), 3.63–3.76 (m, 12H), 3.76–3.97 (m, 4H), 4.05–4.11 (m, 4H), 6.18–6.28 (dd, 4H), 6.70–6.79 (d, 2H); ¹³C NMR (75 MHz, CDCl₃, ppm) δ: 172.93, 150.29, 143.14, 141.21, 117.15, 104.84, 101.13, 75.87, 75.06, 74.62, 74.41, 73.85, 72.73, 70.71, 70.68, 70.65, 70.58, 70.52, 70.31, 70.16, 70.01, 69.84, 69.56, 68.69, 68.49, 67.94, 66.87, 66.16, 65.70, 51.77, 33.65, 18.75, 18.52, 17.91, 16.92, 16.46; IR (NaCl, cm⁻¹): 3362.3, 3036.4, 2970.8, 2929.4, 2874.4, 1966.1, 1723.1, 1617.0, 1515.8, 1455.0, 1407.8, 1376.0, 1354.8, 1274.7, 1230.4, 1198.5, 1123.3, 987.4, 948.8, 837.9, 810.9. MS(EI): m/z 955.5[M]⁺; Anal. calc. for C₄₇H₇₄N₂O₁₈: C, 59.12; H, 7.76; N, 2.94. Found: C, 58.97; H, 7.63; N, 3.12.

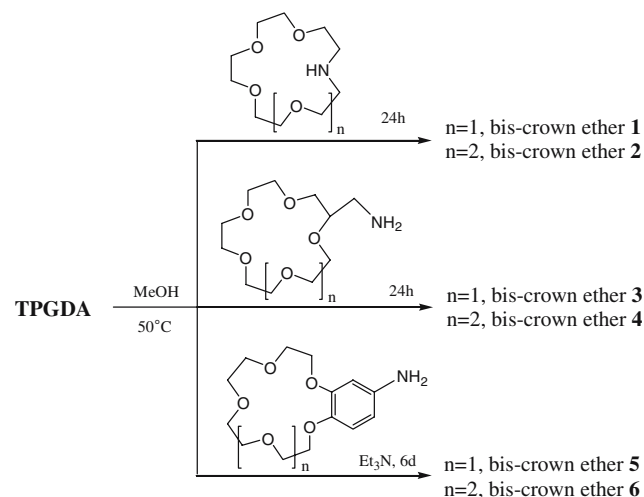
Result and discussion

The approach to the new bis-crown ethers is outlined in Scheme 1. TPGDA contains two active double bonds at both sides of the carbon chain. The primary and secondary amine functional group of 2-aminomethyl crown ethers, 4-aminobenzo crown ethers and 1-aza crown ethers reacted with TPGDA directly in the methanol solution at 50 °C. Since the primary amine group has two proton atoms, the reagent mole ratio of the primary amine group to the double bond should be greater than 1.5:1 to get a high yield of the target product.

The bis-crown ethers **1** and **2** were prepared through Michael addition of TPGDA with 1-aza-15-crown-5 and 1-aza-18-crown-6. Likewise, **3** and **4** were made from TPGDA with 2-aminomethyl-15-crown-5 and 2-aminomethyl-18-crown-6. Bis-crown ethers **5** and **6** were obtained by the similar synthetic route using reaction of TPGDA with 4-aminobenzo-15-crown-5 and 4-aminobenzo-18-crown-6. All the reactions took place under mild condition. The functional groups reacted directly, and only in one step could we obtain the products. The yields were all higher than 70%.

In our previous work [35, 36, 38], 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 need longer time (6 days). These maybe ascribed to the fact that the rich electron benzene ring contains in the 4-aminobenzo crown ethers reduced the activity of the amine group.

In the ¹H NMR spectra, the proton signals of **1–6** could be observed at expected chemical shifts. For example, in the bis-crown ether **1**, the ethereal protons of the crown ether groups appeared as multiplets at δ: 3.47–3.98 ppm. The 1-aza-crown ether CH₂–N–CH₂ proton chemical shift occurred at δ: 2.74–2.78 ppm (triplets). The newly formed CH₂–N bond protons, which connected the TPGDA with the 1-aza-crown ether nitrogen atom, were at δ 2.86–2.91 ppm (triplets).



Scheme 1.

At the δ : 5.8–6.5 ppm region, the double bond proton signals were not found, indicating that the Michael addition accomplished.

The case of **2–6** was all similar to **1**. The benzene ring protons' chemical shift signals of bis-crown ether **5** and **6** were at δ 6.13–6.27 ppm and δ 6.71–6.79 ppm. The –NH proton signals of bis-crown **3–6** were not found as respective peaks in ^1H NMR spectra, and we think they were mixed in the strong intensity peaks of ethereal protons.

The ^{13}C NMR spectra revealed that the removal of the double bond carbon signals which were located around δ : 128 ppm and δ : 131 ppm region. The C=O carbon chemical shift moved from δ : 165 ppm to δ : 173 ppm. The crown ether carbon chemical shifts were seen around δ : 69–70 ppm ranges. The benzene ring carbons of **5** and **6** were found from 150–100 ppm, respectively. All the other carbon atoms' chemical shifts of the bis-crown ethers occurred as expected.

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

The binding interactions of the new host compounds of bis-crown ethers with the alkali metal cations were examined with ^1H NMR spectroscopy and absorption investigation on UV spectrometry.

In the ^1H NMR analysis, the NaSCN, KSCN, RbSCN and CsSCN were dissolved in acetone- d_6 to make a 2×10^{-2} M solution, respectively. **1–6** were dissolved in acetone- d_6 to make 5×10^{-3} M solutions. The gradually downfield shift or upfield shifts were observed with increasing concentration of the alkali metal thiocyanate salt in the bis-crown solution. The stoichiometry of the complexation between the bis-crown ether and the alkali cation was confirmed to be 1:2 by the molar ratio. Small but significant downfield or upfield shifts in the ^1H NMR signals were observed with the addition of the alkali cations were added into the host compounds solution.

As shown in Figure 2, with the addition of NaSCN to bis-crown ether **1** solution, H-1 (O–CO–CH 1_2 –CH 2_2 –N)

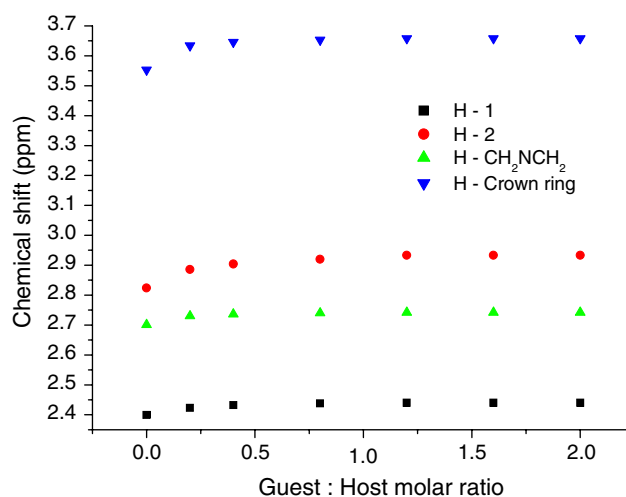


Figure 2. ^1H NMR titration curves for complexation between bis-crown ether **1** and NaSCN in acetone- d_6 .

downfield shifted from δ 2.399 ppm (triplets) (chemical shift δ was relative to TMS δ 0 ppm) to δ 2.440 ppm, $\Delta\delta=0.041$ ppm. H-2 shifted from δ 2.824 ppm (triplets) to δ 2.933 ppm, $\Delta\delta=0.109$ ppm. The chemical shift of 1-aza-crown unit CH $_2$ –N–CH $_2$ -protons downfield shifted from δ 2.701 ppm (triplets) to δ 2.740 ppm, $\Delta\delta=0.039$ ppm. The crown ether ring proton multiple peaks all downshifted, the changed average chemical shift $\Delta\delta=0.103$ ppm, the shape of the peaks became more complicated. The association constants K_a (M^{-1}) was determined by a nonlinear curve-fitting method [45]. The chemical shift change was due to the interaction of crown ether rings with metal cations, which indicates that a new complex was formed. The case of bis-crown ethers **1** and **2** interacted with Na^+ , K^+ , Rb^+ , Cs^+ were similar to the above. The changes of ^1H NMR chemical shifts $\Delta\delta$ of H-1, H-2, 1-aza-crown unit CH $_2$ –N–CH $_2$, the changed crown ring proton chemical shift and the association constant K_a are summarized in Table 1. In the ^1H NMR spectra, the proton signal of the TPGDA ester residues and the methyl groups was not observed evident chemical shift change. We suppose that it was difficult for the ester residues to interact with the metal cations in the low concentrated solution.

In the case of bis-crown ether **3** and **4**, the changes of ^1H NMR chemical shifts $\Delta\delta$ of H-3, H-4 and the changed crown ring proton chemical shift and the

Table 1. Changes of ^1H NMR chemical shifts of bis-crown ethers **1** and **2** with various metal salts

	$\Delta\delta$ of H-1 ^a	$\Delta\delta$ of H-2 ^a	$\Delta\delta$ of CH $_2$ –N–CH $_2$	$\Delta\delta$ of crown H	K_a
1 + NaSCN	0.041	0.109	0.039	0.103	735 \pm 24
1 + KSCN	0.044	0.111	0.069	0.095	340 \pm 16
1 + RbSCN	0.026	0.040	0.045	0.059	195 \pm 13
1 + CsSCN	0.015	0.035	0.053	0.039	75 \pm 5
2 + KSCN	0.043	–0.030	0.089	0.059	595 \pm 16
2 + RbSCN	0.035	0.011	0.088	0.056	554 \pm 15
2 + CsSCN	0.031	–0.041	–0.050	0.053	136 \pm 4

^aH-1 and H-2 are protons (O–CO–CH 1_2 –CH 2_2 –N) in bis-crown ethers **1–2**.

association constant K_a are summarized in Table 2. See also Figure 3.

In the case of bis-crown ether **5** and **6**, the changes of ^1H NMR chemical shifts $\Delta\delta$ of H-5 to H-12 and the K_a are summarized in Table 3.

Alkali metal picrates have been employed frequently to estimate the interaction between the alkali metal cations with the host compounds [46, 47]. In the absorption investigation of UV spectrum, the new bis-crown ethers were made into 2×10^{-3} M solutions in methanol. The sodium picrate, potassium picrate and cesium picrate were dissolved in methanol to make 3.5×10^{-4} M solutions, respectively. The absorption maximum of the picrate anion in methanol was observed at 354 nm. Interestingly, with the addition of the bis-crown ether solution into the alkali picrate salt solutions, the absorption intensity at 354 nm increased. As shown in the Figure 4, with the addition of the bis-

crown ether **1** to Kpicrate methanol solution, the absorption intensity at 354 nm increased. The increased ratio of the absorbance intensity was different. The increased intensity order are outlined in Table 4. The results indicate that interactions of the new host bis-crown ethers with the guest alkali metal cations of Na^+ , K^+ and Cs^+ have taken place in the methanol solution.

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

Conclusion

In this paper, we have successfully used the Michael addition reaction to synthesize the novel bis-crown ethers from the 1-aza crown ethers, 2-aminomethyl crown ethers and 4-aminobenzo crown ethers with TPGDA. The structure is novel. The approach is efficient. The reaction can take place directly without protection-deprotection under gentle condition in good yields. The interaction between the bis-crown ethers and alkali metal cations such as Na^+ , K^+ , Rb^+ and Cs^+ was investigated. The result showed that the new bis-crown ethers can capture not only the ideal size metal cations Na^+ and K^+ , but also larger size cations than that of the crown ether ring cavity like Rb^+ and Cs^+ to form sandwich type complexes.

Table 2. Changes of ^1H NMR chemical shifts of bis-crown ethers **3** and **4** with various metal salts

	$\Delta\delta$ of H-3 ^a	$\Delta\delta$ of H-4 ^a	$\Delta\delta$ of crown H	K_a
3 + NaSCN	0.037	0.095	0.078	741 ± 49
3 + KSCN	0.038	0.147	0.063	542 ± 17
3 + RbSCN	0.053	0.125	0.061	427 ± 16
3 + CsSCN	0.036	0.099	0.055	276 ± 11
4 + KSCN	0.003	0.067	0.072	650 ± 15
4 + RbSCN	0.002	0.066	0.060	471 ± 16
4 + CsSCN	0.003	0.057	0.062	145 ± 18

^aH-3 and H-4 are the protons in bis-crown ether **3** and **4** as indicated in Figure 3(A).

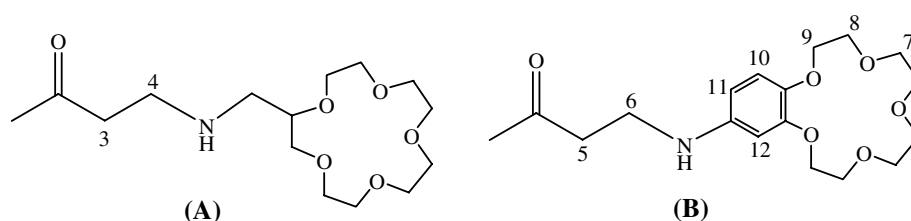


Figure 3. The proton number indicated in the bis-crown **3**–**6**.

Table 3. Changes of ^1H NMR chemical shifts of bis-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	K_a
5 + NaSCN	0.003	0.012	0.042	0.051	0.103	0.103	0.084	0.066	957 ± 26
5 + KSCN	0.024	0.031	0.053	0.032	-0.014	-0.002	-0.030	0.058	792 ± 16
5 + RbSCN	0.020	0.022	0.049	0.027	0.023	0.029	-0.027	0.054	353 ± 17
5 + CsSCN	0.009	0.014	0.007	0.032	0.047	0.040	0.030	0.033	308 ± 24
6 + KSCN	0.004	0.013	0.049	0.091	0.112	0.086	0.118	0.052	460 ± 18
6 + RbSCN	0.010	0.014	0.049	0.038	0.090	0.074	0.082	0.050	286 ± 13
6 + CsSCN	0.005	0.012	0.048	0.033	0.084	0.103	0.108	0.050	176 ± 9

^aH-5 to H-12 are the protons of in bis-crown ether **5** and **6** as indicated in Figure 3(B).

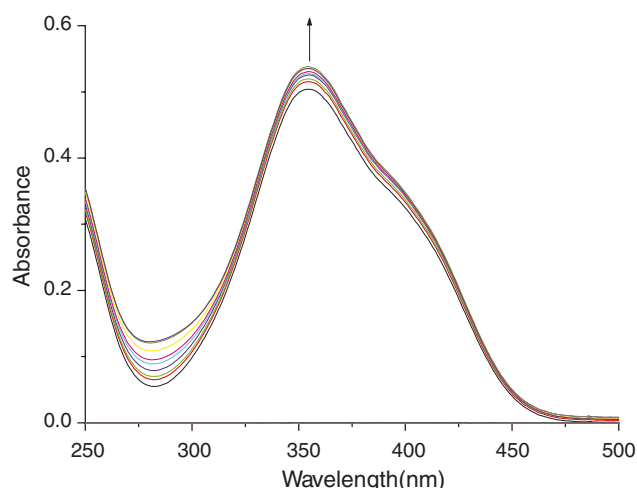


Figure 4. The UV spectrum of Kpicrate with the addition of the bis-crown ether **1** in methanol.

Table 4. The increased absorbance order of the bis-crown ethers interacted with alkali metal picrate salts in MeOH solution

Bis-crown ether	The increased absorbance order of the cations
Bis-crown ether 1	$\text{Na}^+ < \text{K}^+ < \text{Cs}^+$
Bis-crown ether 2	$\text{Na}^+ < \text{K}^+ < \text{Cs}^+$
Bis-crown ether 3	$\text{Na}^+ < \text{K}^+ < \text{Cs}^+$
Bis-crown ether 4	$\text{Na}^+ < \text{K}^+ < \text{Cs}^+$
Bis-crown ether 5	$\text{Na}^+ < \text{K}^+ < \text{Cs}^+$
Bis-crown ether 6	$\text{Na}^+ < \text{K}^+ < \text{Cs}^+$

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