



## Synthesis and Ion Recognition Exploration of Novel Benzothiazolyl Modified Crown Ethers

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Four novel benzothiazolyl modified crown ethers, non-cyclic crown ethers (podands) **1** and **2**, 4-(2-benzothiazole)benzo-15-crown-5 (**3**) and dibenzothiazole dibenzo-18-crown-6 (**4**) were synthesized from 2-aminobenzenethiol. The photophysical behaviour and the binding ability of **1-4** with some alkali metal and alkaline earth metal cations were investigated by UV-VIS spectrometry. The result obtained indicates that **4** displays high selectivity to potassium ion.

**Key Words:** Synthesis, Modified crown ethers, Coordination, Ion recognition.

### INTRODUCTION

Host-guest chemistry has been attracting widespread attention in the past several decades, which has led to the reinforcement of interest in crown ether chemistry<sup>1-3</sup>. Crown ethers can be taken as molecular receptors to selectively bind ionic or molecular guests forming host-guest complexes or supramolecular species. Therefore, numerous efforts have been contributed to design and synthesis of functional crown ethers derivatives in order to enhance their original ionic/molecular binding affinities and selectivities<sup>4-10</sup>. A large number of examples of molecular and ion recognition have been reported. Burdette *et al.*<sup>11</sup> demonstrated a modular approach for preparing nitrobenzhydryl derived crown cages that can be as chemosensors for magnesium ion. A novel fluorescent chemosensor composed of biarylpyridine and crown ether moieties has been reported<sup>12</sup> to selectively identify alkali metals and alkaline earth metal cations *via* twisted intramolecular charge transfer. It is known that the conformation of open-chain crown ethers can change drastically from a linear structure to a pseudocyclic structure upon complex formation with metal ions. A water soluble non-cyclic compound containing amino naphthalimide groups possessed high selectivity and sensitivity for Hg<sup>2+</sup>.<sup>13</sup> An open-chain polyether dicarboxylic acid ionophore could effectively extract Pb<sup>2+</sup> from weakly acidic aqueous solutions<sup>14</sup>. Herein, we report the synthesis and characterization of four new benzothiazolyl modified crown ethers (**1** and **2** are open-chain crown ethers) and also their UV-Visible behaviour upon complexation with alkali/alkaline earth metal ions. Comparison of the spectra behaviour of these

four compounds with that of the parent analogue **5** (Chart-1) will further our understanding of the luminescent origin upon complexation with cations. Our particular interest is to investigate how the benzothiazolyl groups affect the spectral behaviour of these compounds upon complexation with metal ions.

### EXPERIMENTAL

Diethyleneglycol di(toluenep-sulfonate)<sup>15</sup>, triethyleneglycol di(toluenep-sulfonate)<sup>15</sup>, 4-(benzo[d]thiazol-2-yl)-2-methoxyphenol<sup>16</sup>, 4-carbaldehyde benzo-15-crown-5 and dicarbaldehyde dibenzo-18-crown-6<sup>12</sup> were prepared according to the literature procedures. Unless otherwise stated, all reactions were carried out without taking precautions to exclude air and moisture. All solvents and chemicals were purchased from commercial sources and used as received unless stated otherwise. All reaction temperatures refer to bath temperatures. <sup>1</sup>H NMR spectra were recorded on a Bruker 400 MHz spectrometer. IR spectra were conducted on Bruker vector 22 spectrometer. Elemental analyses were performed on a Perkin-Elmer-2400C instrument. UV-VIS absorption spectra were recorded on a Phenix UV1901PC spectrophotometer.

#### Synthesis procedure

**Open-chain crown ether (1):** A solution of 4-(benzo[d]thiazol-2-yl)-2-methoxyphenol (0.26 g, 1 mmol) and potassium carbonate (0.17 g, 1.2 mmol) in DMF (5 mL) was stirred at 20 °C for 2 h, then diethyleneglycol di(toluenep-sulfonate) (0.21g, 0.5 mmol) in 4 mL DMF was dropped into it. The whole solution was heated to 80 °C and stirring for

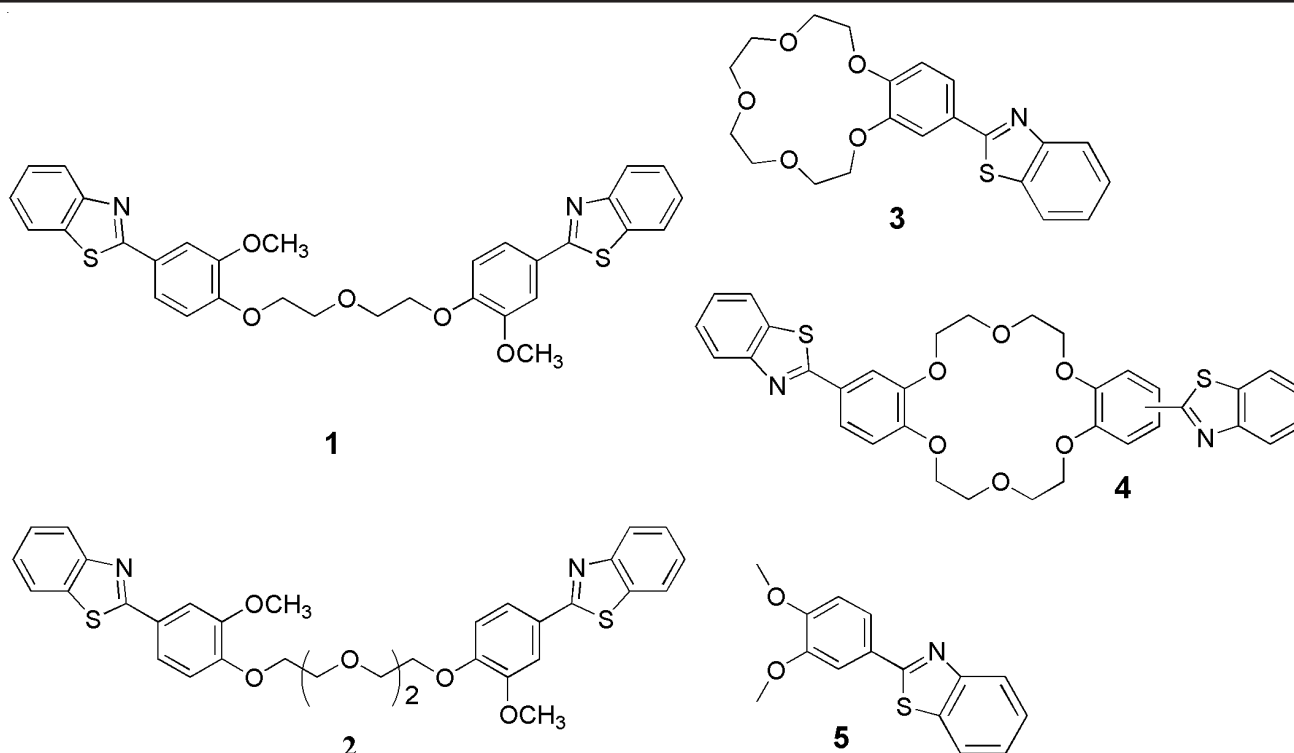


Chart-1: Structures of compounds 1-5

30 h. After cooling, the resultant mixture was poured into ice water and was kept in the refrigerator for 2 days. The yellow solid was filtered and washed three times with ice-water and then dried in a vacuum oven to give the final product with a yield of 75 %. m.p.: 183-186 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ in ppm) 3.989 (s, 6H), 4.010-4.034 (t, 4H), 4.285-4.309 (t, 4H), 6.981-7.002 (d, 2H), 7.260 (s, 2H), 7.324-7.362 (t, 2H), 7.443-7.547 (m, 2H), 7.695-7.699 (d, 2H), 7.827-7.847 (d, 2H), 8.008-8.028 (d, 2H). IR (KBr, ν<sub>max</sub>, cm<sup>-1</sup>): 3355, 2923, 1602, 1532, 1488, 1432, 1268, 1128, 1012, 869, 755, 647. Anal. calcd. for C<sub>32</sub>H<sub>28</sub>N<sub>2</sub>O<sub>5</sub>S<sub>2</sub>: C, 65.43; H, 4.83; N, 4.79. Found: C, 65.25; H, 4.74; N, 4.68.

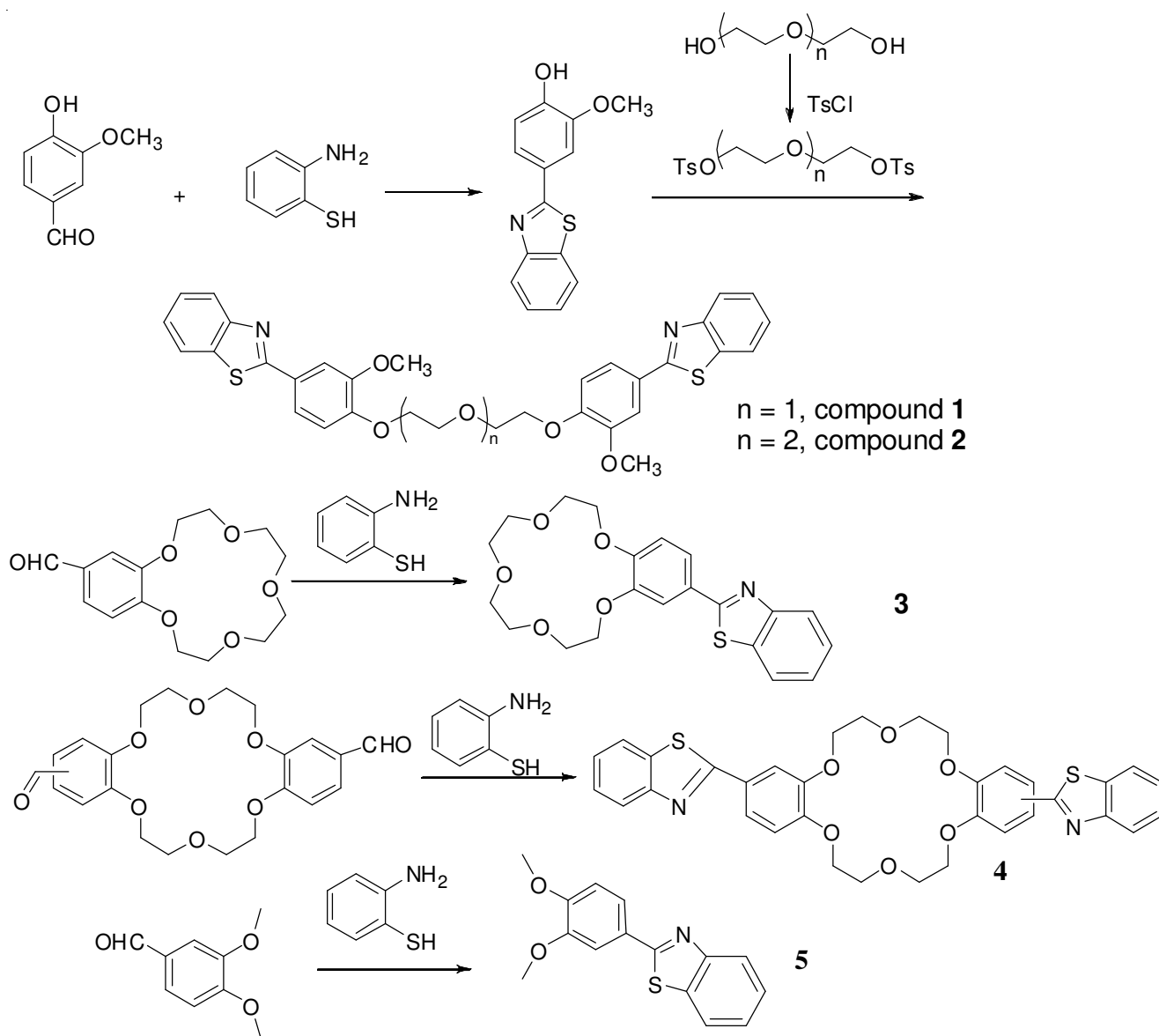
**Open-chain crown ether (2):** The procedure was similar to the preparation of open-chain crown ether (1). Desired product was light yellow solid with a yield of 86 %. m.p.: 138-140 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ in ppm) 3.782 (s, 4H), 3.930-3.956 (t, 4H), 3.982 (s, 6H), 4.240-4.266 (t, 4H), 6.952-6.973 (d, 2H), 7.261 (s, 2H), 7.443-7.547 (m, 2H), 7.440-7.532 (m, 2H), 7.688-7.693 (d, 2H), 7.827-7.848 (d, 2H), 8.007 (d, 2H). IR (KBr, ν<sub>max</sub>, cm<sup>-1</sup>): 3442, 2873, 1600, 1523, 1482, 1450, 1265, 1147, 1035, 1008, 867, 761, 553. Anal. calcd. for C<sub>34</sub>H<sub>32</sub>N<sub>2</sub>O<sub>6</sub>S<sub>2</sub>: C, 64.95; H, 5.13; N, 4.46. Found: C, 64.81; H, 5.32; N, 4.30.

**4-(2-benzothiazole)benzo-15-crown-5 (3):** A mixture of 4-carbaldehyde benzo-15-crown-5 (0.21 g, 0.71 mmol) and 2-aminobenzenethiol (0.13 g, 1.04 mmol) in 10 mL anhydrous methanol was refluxed for 8 h. Then the resultant mixture was cooled to room temperature. After filtering the precipitate, the filtrate was evaporated to dry under reduced pressure. The retained crude product was recrystallized with ethyl acetate to give a yellow crystal solid with a yield of 25 %. m.p.: 113-119 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ in ppm) 3.784 (s, 8H), 3.940-

3.961 (m, 4H), 4.193-4.214 (t, 2H), 4.282-4.304 (t, 2H), 6.915-6.935 (d, 1H), 7.361-7.379 (d, 1H), 7.454-7.493 (q, 1H), 7.580-7.606 (q, 1H), 7.720 (s, 1H), 7.862-7.882 (d, 1H), 8.030 (s, 1H). IR (KBr, ν<sub>max</sub>, cm<sup>-1</sup>): 3423, 3057, 2929, 2873, 1600, 1480, 1426, 1280, 1140, 923, 756, 749, 700. Anal. calcd. for C<sub>21</sub>H<sub>23</sub>NO<sub>5</sub>S: C, 62.83; H, 5.77; N, 3.49. Found: C, 62.59; H, 5.62; N, 3.40.

**Dibenzothiazole dibenzo-18-crown-6 (4):** A mixture of dicarbaldehyde dibenzo-18-crown-6 (4.16 g, 10 mmol) and 2-aminobenzenethiol (2.50 g, 20 mmol) in 20 mL anhydrous methanol was refluxed for 8 h. Then the resultant mixture was cooled to room temperature. A pale yellow precipitate was filtered and washed three times with cold ethanol. The retained crude product was recrystallized with ethyl acetate to give a yellow crystal with a yield of 10 %. m.p.: 243-245 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ in ppm) 4.085-4.093 (d, 8H), 4.249-4.272 (t, 4H), 4.332-4.355 (t, 4H), 6.925-6.946 (d, 2H), 7.347-7.367 (q, 2H), 7.446-7.470 (q, 2H), 7.577-7.582 (d, 2H), 7.597-7.602 (d, 2H), 7.700-7.712 (t, 2H), 7.854-7.881 (q, 2H). IR (KBr, ν<sub>max</sub>, cm<sup>-1</sup>): 3421, 3053, 2925, 2875, 2353, 1731, 1589, 1488, 1423, 1265, 1137, 1052, 921, 751, 643. Anal. calcd. for C<sub>34</sub>H<sub>30</sub>N<sub>2</sub>O<sub>6</sub>S<sub>2</sub>: C, 65.16; H, 4.82; N, 4.47. Found: C, 65.35; H, 4.68; N, 4.99.

**2-(3,4-Dimethoxybenzene)benzothiazole (5):** The procedure was similar to that described for the preparation of 4-(2-benzothiazole)benzo-15-crown-5. Desired product was yellow solid with a yield of 65.2 %. m.p.: 136-138 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ in ppm) 3.956 (s, 3H), 4.023 (s, 3H), 6.936-6.957 (d, 1H), 7.338-7.376 (t, 1H), 7.452-7.491 (q, 1H), 7.590-7.615 (q, 1H), 7.713-7.718 (d, 1H), 7.864-7.884 (d, 1H), 8.025-8.046 (d, 1H). IR (KBr, ν<sub>max</sub>, cm<sup>-1</sup>): 2964, 2839, 1591, 1523, 1481, 1424, 1262, 1142, 1015, 867, 813, 763,



Scheme-I: Syntheses route of compounds 1-5

693, 653. Anal. calcd. for  $C_{15}H_{13}NO_2S$ : C, 66.40; H, 4.83; N, 5.16. Found: C, 66.26; H, 4.70; N, 5.29.

**Detection method:** UV-VIS spectra were measured using a conventional quartz cell ( $10 \times 10 \times 45$  mm) at  $25^\circ\text{C}$  on a Phenix UV1901PC spectrophotometer. In these experiments, alkali metals and alkaline earth metal perchlorates were chosen as the object cations and the methanol/water (4:1) and DMF were selected as the solvents. The titration solutions were prepared in 10 mL volumetric flasks with the guest/host molar ratio ranging from 0 to *ca.* 200.

## RESULTS AND DISCUSSION

Our synthesis began with 2-aminobenzenethiol. The intermediates 4-(benzo[d]thiazol-2-yl)-2-methoxyphenol, 4-carbaldehyde benzo-15-crown-5, dicarbaldehyde dibenzo-18-crown-6 as well as compound **5** were prepared according to the literature procedures. Treating 2-aminobenzenethiol with several aldehyde in anhydrous methanol afforded **3-5** in low to medium yield (Scheme-I). However, **1** and **2** were obtained in good yields by treating firstly 2-aminobenzenethiol and

4-hydroxy-3-methoxybenzaldehyde, then reacting with diethylene glycol di(toluene-*p*-sulfonate) and triethylene glycol di(toluene-*p*-sulfonate) respectively. For the crown ether **4**, no efforts were made to separate the two positional isomerizations.

The UV spectra of the compounds **1-5** in DMF are shown in Fig. 1. It can be seen from the figure, the spectra of the compounds **1-4** are similar to that of **5**, have absorptions at about 328-330 nm. When excesses equivalent alkali metal and alkaline earth metal cations were added to the DMF solution of **1** and **2**, no significant changes were observed in their UV-VIS spectra. The same results were obtained in the replacement of **1** by compound **3** and **5**. Interestingly, different from other compounds and cations, a large increase of the peak was shown in the UV-VIS spectra of **4** upon binding of  $K^+$  (Fig. 2). In the spectrum titration experiments, the fluorescence intensity of **4** gradually increased with increasing guest concentration as shown in Fig. 2. One reasonable explanation for this observation is the good complementarity between the cavity of 18-crown-6 in **4** and the ionic radii of potassium ion.

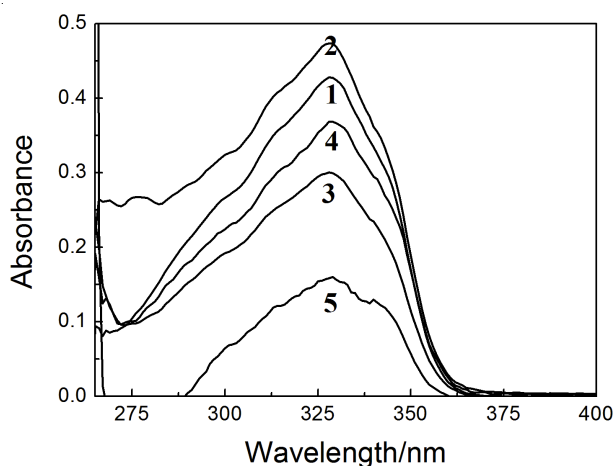


Fig. 1. UV-VIS spectra of compounds 1-5 ( $1 \times 10^{-5}$  M) in DMF at 25 °C

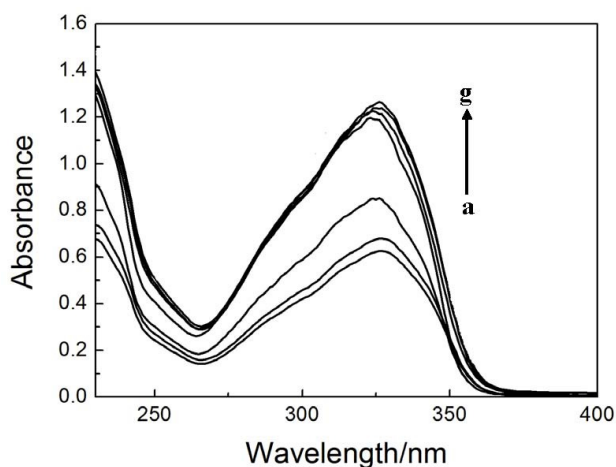


Fig. 2. UV-VIS spectral changes of compound 4 ( $2 \times 10^{-5}$  M) upon addition of potassium perchlorate ( $0-4 \times 10^{-3}$  M, a-g) in 4:1 Methanol- $H_2O$  solution at 25 °C

### Conclusion

In summary, four non-cyclic and cyclic crown ethers possessing single or double benzothiazolyl groups have been

synthesized and characterized. Because of the good complementarity between the cavity of 18-crown-6 in **4** and the ionic radii of  $K^+$ , the crown ether **4** showed the responses specific for  $K^+$ . On the basis of the above findings, further investigation on the binding abilities of these compounds upon transition metal cations are currently in progress.

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