

## CHAPTER II

### EXPERIMENTAL

#### 2.1 Synthesis of Calix[4]arene Derivatives

##### Chemicals

- |                               |                                      |
|-------------------------------|--------------------------------------|
| 1. Acetone                    | Commercial grade, Mallinckrodt, USA. |
| 2. Acetonitrile               | Analar grade, J.T. Baker, USA.       |
| 3. 1,4-Diaminobutane          | Analar grade, sigma, USA.            |
| 4. 1,3-Diaminopropane         | Analar grade, Fluka, Switzerland     |
| 5. 1,2-Dibromoethane          | Analar grade, Merck, Germany         |
| 6. Dichloromethane            | Analar grade, J.T. Baker, USA.       |
| 7. Diethylene triamine        | Analar grade, BDH, England           |
| 8. Dimethylsulfate            | Analar grade, Merck, Germany         |
| 9. Diphenylether              | Analar grade, Fluka, Switzerland     |
| 10. Ethyl acetate             | Analar grade, J.T. Baker, USA.       |
| 11. Formaldehyde solution 37% | Analar grade, Merck, Germany         |
| 12. Hydrochloric acid         | Analar grade, J.T. Baker, USA.       |
| 13. Methanol                  | Analar grade, J.T. Baker, USA.       |
| 14. Methyl iodide             | Analar grade, Fluka, Switzerland     |
| 15. Potassium carbonate       | Analar grade, Merck, Germany         |
| 16. Salicylaldehyde           | Analar grade, Fluka, Switzerland     |
| 17. Sodium borohydride        | Analar grade, Fluka, Switzerland     |

- |                                 |                                  |
|---------------------------------|----------------------------------|
| 18. Sodium hydroxide            | Analar grade, Merck, Germany     |
| 19. 4- <i>tert</i> -butylphenol | Analar grade, Fluka, Switzerland |
| 20. Tetraethylene pentamine     | Analar grade, Sigma, USA.        |
| 21. Tetrahydrofuran             | Analar grade, J.T. Baker, USA.   |
| 22. Toluene                     | Analar grade, J.T. Baker, USA.   |
| 23. Triethylene tetramine       | Analar grade, Sigma, USA.        |

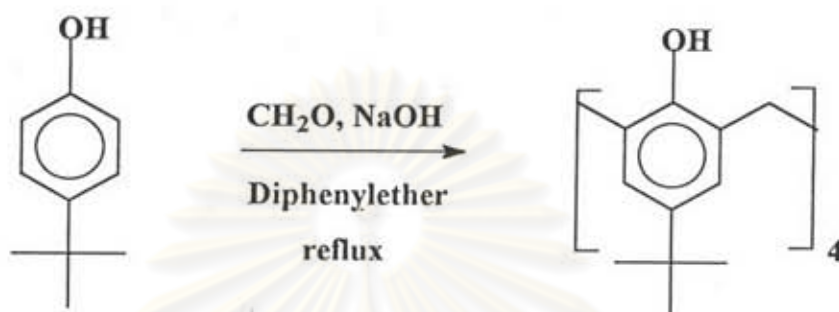
### Apparatus

1. Buchi 500 Melting Points Apparatus, Buchi, Switzerland
2. CHNO/S Analyser PE2400 Series II, Perkin Elmer, USA.
3. Eyela Magnetic Stirrer RC-2, Eyela, Japan
4. Fourier Transform NMR Spectrometer ACF 200 MHz, Bruker, Switzerland
5. Fourier Transform NMR Spectrometer 500 MHz, Jeol, Japan
6. Mass Spectrometer (MS), VG TRIO 2000, Fisons, England
7. Rotary Evaporator, Eyela, Japan
8. Vacuum-system B-169, Buchi, Switzerland

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## Experimental Section

### 2.1.1 Preparation of *p*-*tert*-butylcalix[4]arene (1) [42]



To a 500 mL Erlenmeyer flask was added 25.00 g (166.25 mmol) of *p*-*tert*-butylphenol, 15.60 mL of 37% formaldehyde solution (207.50 mmol of HCHO) and 0.30 g (7.50 mmol) of NaOH (corresponding to 0.05 equiv. of phenol) dissolved in a minimum amount of H<sub>2</sub>O. The contents of the flask were heated in an oil bath until the solution became solid, maintaining the temperature of the bath at 110-120°C. During this period, the reaction mixture which was clear at the beginning became viscous and turned orange at first and then changed to a thick yellow mass. At this point, the flask was removed from the heating bath and allowed to cool to room temperature. The residue was broken into small pieces. The precursor (which can also be made directly in a two-necked flask) was then suspended in 200 mL of diphenyl ether in 1-L two-necked flask equipped with a dean an stark, condenser, and mechanical stirrer under nitrogen atmosphere. The contents of the flask were heated with heating mantle. During the first phase of the reaction, as the yellow precursor went into solution, the condenser was left off to remove some water. The condenser was put in place and the contents of the flask were refluxed for

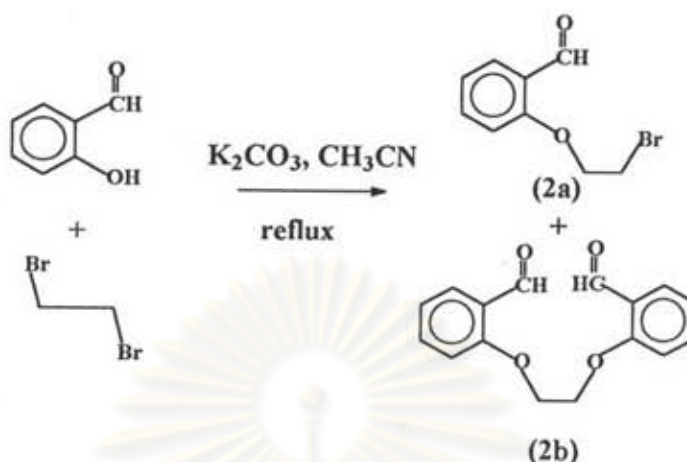
1.5 h. During this phase of the reaction the initial precipitate disappeared to give a clear solution. The reaction mixture was then cooled to room temperature, treated with 250 mL of ethyl acetate, stirred for 20 min. and allowed to stand for 30 min. Filtration yields material which was washed twice with 25 mL of ethyl acetate and once with 50 mL of acetic acid to yield 20.30 g of crude product. Recrystallization from toluene gave 16.50 g (60%) of product as glistening white plates, Mp. 342-344 °C.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) spectrum is shown in Figure A.1 and  $^1\text{H-NMR}$  spectral analysis is shown in Table 3.1. Mass spectroscopy ( $\text{EI}^+$ , 20ev) is shown in Figure A.20, 648 (100%). Anal. Calcd for  $\text{C}_{44}\text{H}_{56}\text{O}_4 \cdot \text{C}_7\text{H}_8$ ; C, 83.66%; H, 8.70%. Found: C; 82.91%; H, 8.70%.



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## 2.1.2 Preparation of 2[(1-formyl-2-phenyl)oxy]ethylbromide (2a)

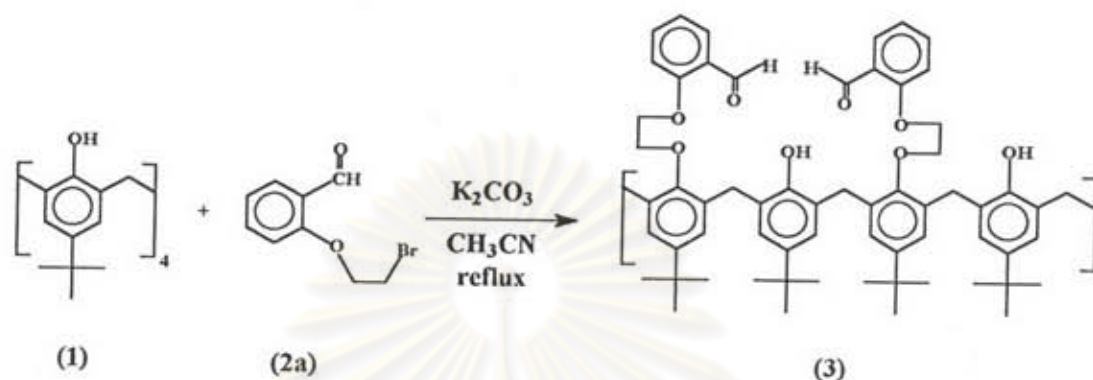
[43]



Into a 1-L 2-necked round bottom flask was added acetonitrile (250 mL), salicylaldehyde (14.80 g, 121.20 mmol), potassium carbonate (23.00 g, 167.40 mmol) and 1,2-dibromoethane (224.00 g, 110.0 mmol). After the reaction mixture was refluxed under nitrogen atmosphere for 4 hours, it was cooled to room temperature and filtered. The filtrate was concentrated on a rotary evaporator to yield a yellowish oily residue (36.55 g). The residue was chromatographed on a silica column (400 g) with dichloromethane as eluent. The 2-[(1-formyl-2-phenyl)oxy]ethylbromide (2a) fraction was collected with the unreacted salicylaldehyde fraction and the collected fractions were evaporated to yield the product upon addition of hexane. The precipitate was filtered and washed with hexane. Yield: 14.00 g (51%). <sup>1</sup>H-NMR (CDCl<sub>3</sub>) spectrum is shown in Figure A.2 and <sup>1</sup>H-NMR spectral analysis is shown in Table 3.2.

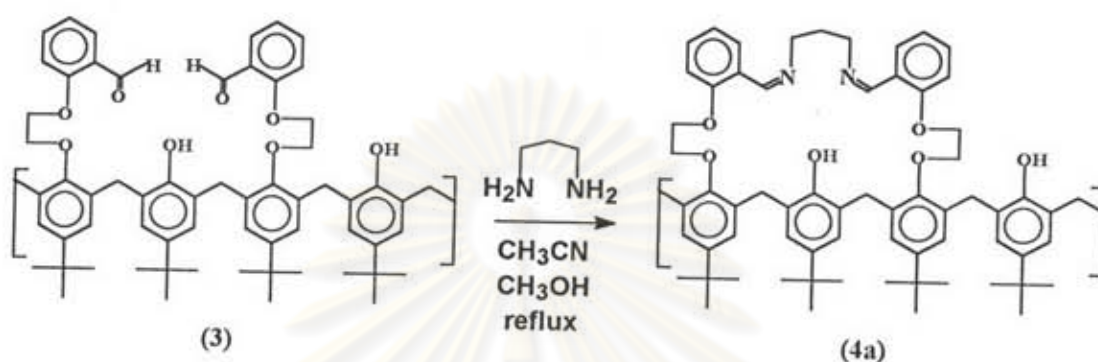
The second product eluted was pure 2,2'-(1,1'-dioxoethane)bisbenzaldehyde (2b) which solidified upon evaporation (0.58 g). <sup>1</sup>H-NMR (CDCl<sub>3</sub>) spectrum is shown in Figure A.3 and <sup>1</sup>H-NMR spectral analysis is shown in Table 3.3.

### 2.1.3 Preparation of 25,27-bis[2-[(1-formyl-2-phenyl)oxy]ethyl]-*p*-*tert*-butylcalix[4]arene (3) [43]



Into a 1-L 2-necked round bottom flask was added *p*-*tert*-butyl-calix[4]arene (1) (11.70 g, 18.10 mmol), potassium carbonate (20.00 g, 145.60 mmol) and acetonitrile (350 mL). A solution of 2-[(1-formyl-2-phenyl)oxy]ethylbromide (2a) (9.53 g, 41.70 mmol) in acetonitrile (150 mL) was then slowly dropped into the solution. The reaction mixture was refluxed under nitrogen for 63 h. After cooling to room temperature, potassium carbonate was filtered off and washed with a large amount of acetone and dichloromethane and precipitated by addition of methanol yielding the pure 25,27-bis[2-[(1-formyl-2-phenyl)oxy]ethyl]-*p*-*tert*-butylcalix[4]arene (3). Yield: 11.80 g (67%).  $^1\text{H-NMR}$  (  $\text{CDCl}_3$  ) spectrum is shown in Figure A.4 and  $^1\text{H-NMR}$  spectral analysis is shown in Table 3.4.

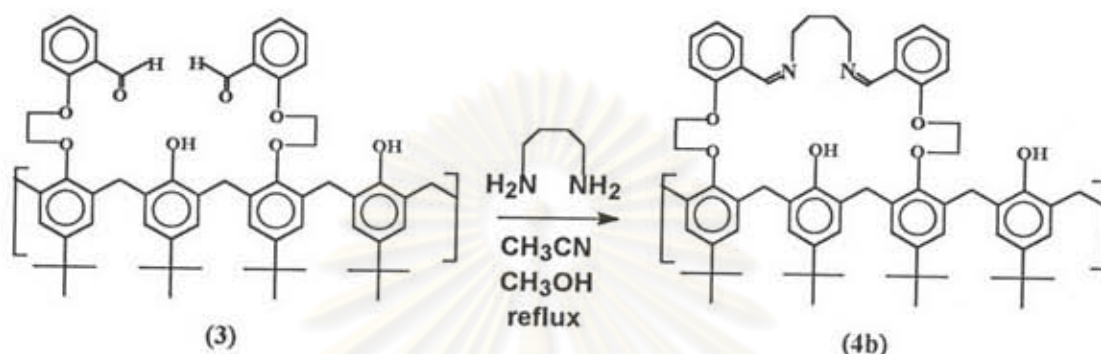
2.1.4 Preparation of 25,27-[2,2'-[1,1'-(1,3-propylenediimino)-2,2'-diphenoxy]diethyl]-*p*-*tert*-butylcalix[4]arene (4a) [43]



25,27-*bis*[2-[(1-formyl-2-phenyl)oxy]ethyl]-*p*-*tert*-butylcalix[4]arene (3) (2.88 g, 3.10 mmol) and acetonitrile (250 mL) were put in a 500 mL 2-necked round bottom flask. After complete dissolution of (3), 1,3-diaminopropane (0.28 mL, 3.40 mmol) in methanol (50 mL) was added dropwise into the solution. The reaction mixture was refluxed under nitrogen atmosphere for 9 h to afford a white precipitate. The precipitate was filtered and washed with methanol. Yield: 2.43 g (86%).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) spectrum is shown in Figure A.5 and  $^1\text{H-NMR}$  analysis is shown in Table 3.5.

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2.1.5 Preparation of 25,27-[2,2'-[1,1'-(1,4-butylenediimino)-2,2'-diphenoxy]diethyl]-*p*-*tert*-butylcalix[4]arene (4b) [43]

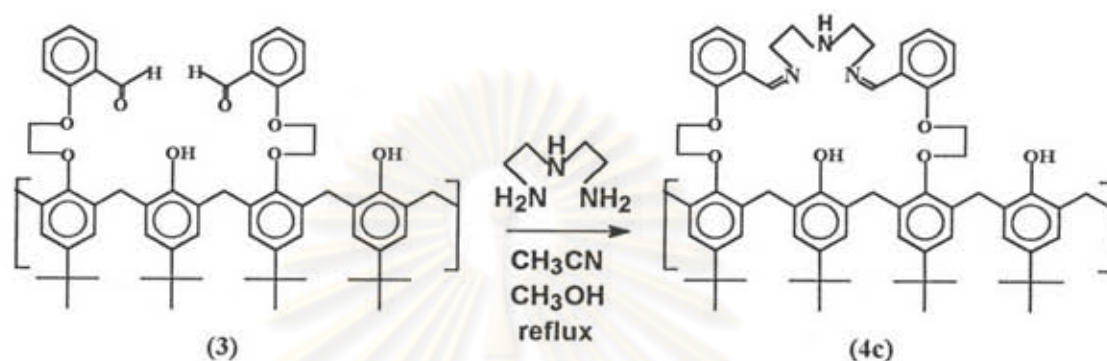


Into a 500 mL 2-necked round bottom flask was added 25,27-*bis*[2-[(1-formyl-2-phenyl)oxy]ethyl]-*p*-*tert*-butylcalix[4]arene(3) (3.00g, 3.18 mmol) and acetonitrile (250 mL). After dissolution of (3), 1,4-diaminobutane (0.34 mL, 3.40 mmol) in methanol (50 mL) was added dropwise into the solution. The reaction mixture was refluxed under nitrogen atmosphere for 9 h to afford a white precipitate. The precipitate was filtered and washed with methanol. Yield: 2.68 g (88%).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) spectrum is shown in Figure A.6 and  $^1\text{H-NMR}$  analysis is shown in Table 3.6.

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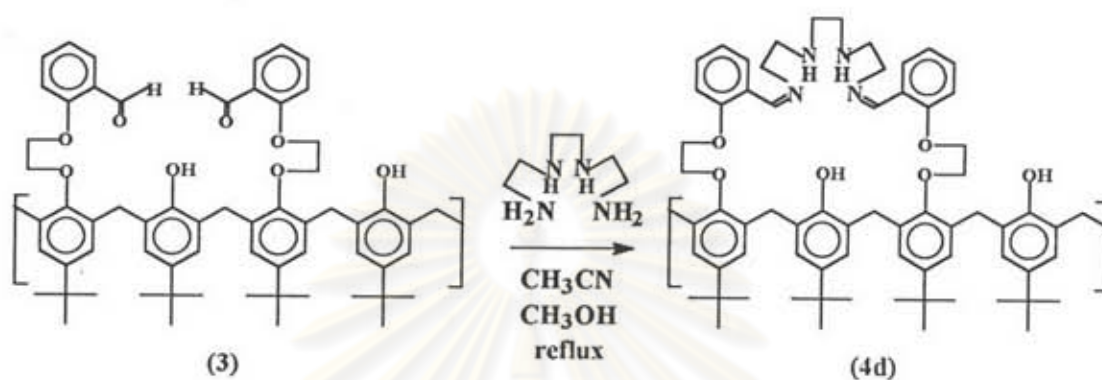


2.1.6 Preparation of 25,27-[2,2'-[(1,1'-(1,5-(3-aza)pentylene)diimino)-2,2'-diphenoxy]diethyl]-*p*-*tert*-butylcalix[4]arene (4c)



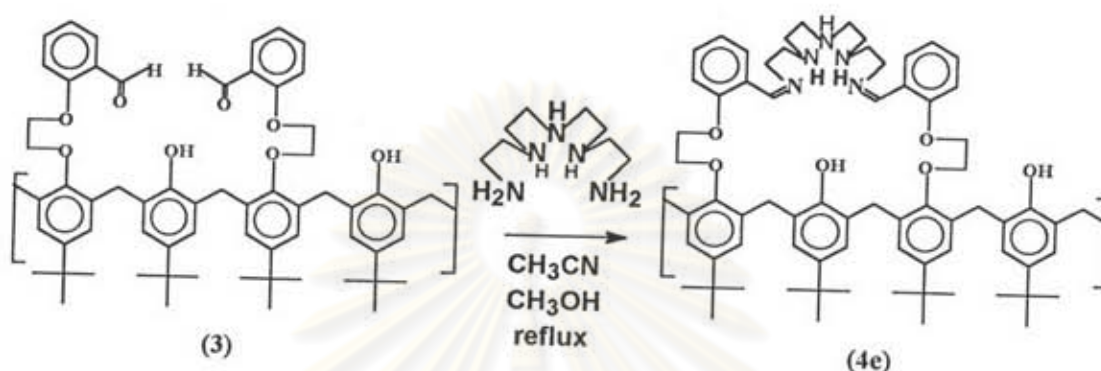
Into a 500 mL 2-necked round bottom flask was added 25,27-bis[2-[(1-formyl-2-phenyl)oxy]ethyl]-*p*-*tert*-butylcalix[4]arene (3) (3.00 g, 3.10 mmol) and acetonitrile (250 mL). After dissolution of (3), diethylene triamine (0.36 g, 3.90 mmol) in methanol (50 mL) was added dropwise into the solution. The reaction mixture was refluxed under nitrogen atmosphere for 9 h to afford a white precipitate. The precipitate was filtered and washed with methanol. Yield: 3.01 g (97 %). Mp. 251-252°C (decomp.).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) spectrum is shown in Figure A.7 and  $^1\text{H-NMR}$  spectral analysis is shown in Table 3.7. Mass spectrum ( $\text{FAB}^+$ ) is shown in Figure A.21, 1012.3 (100 %). Anal. Calcd for  $\text{C}_{66}\text{H}_{81}\text{O}_6\text{N}_3$ ; C, 77.76%; H, 8.70%; N, 4.12%. Found: C, 77.69%; H, 8.09%; N, 4.19%.

2.1.7 Preparation of 25,27-[2,2'-[(1,1'-(1,9-(3,6-diaza)octylene) diimino)-2,2'-diphenoxy]diethyl]-*p*-*tert*-butylcalix[4]arene (4d)



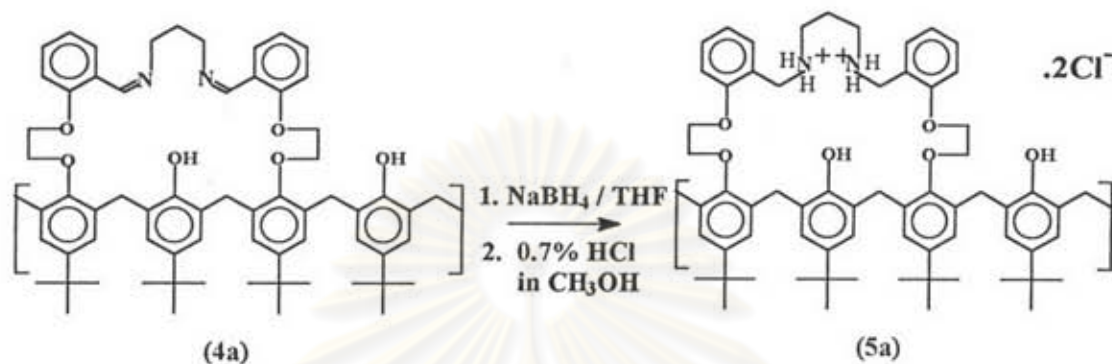
Into a 500 mL 2-necked round bottom flask was added 25,27-bis[2-[(1-formyl-2-phenyl)oxy]ethyl]-*p*-*tert*-butylcalix[4]arene (3) (3.00 g, 3.18 mmol) and acetonitrile (250 mL). After dissolution of (3), triethylene tetramine (0.51 g, 3.50 mmol) in methanol (50 mL) was added dropwise into the solution. The reaction mixture was refluxed under nitrogen atmosphere for 9 h to afford a yellow precipitate. The precipitate was filtered and washed with acetonitrile. Yield: 0.85 g (24%). Mp. 248 °C (decomp.). <sup>1</sup>H-NMR (CDCl<sub>3</sub>) spectrum is shown in Figure A.8 and <sup>1</sup>H-NMR analysis is shown in Table 3.8. Anal. Calcd for C<sub>68</sub>H<sub>86</sub>O<sub>6</sub>N<sub>4</sub>·CH<sub>3</sub>OH; C, 76.21%; H, 8.34%; N, 5.15%. Found: C, 76.14%; H, 8.26%; N, 4.68%.

2.1.8 Preparation of 25,27-[2,2'-[(1,1'-(1,11-(3,6,9-triaza)undecylene) diimino)-2,2'-diphenoxy]diethyl]-*p*-*tert*-butylcalix[4]arene (4e)



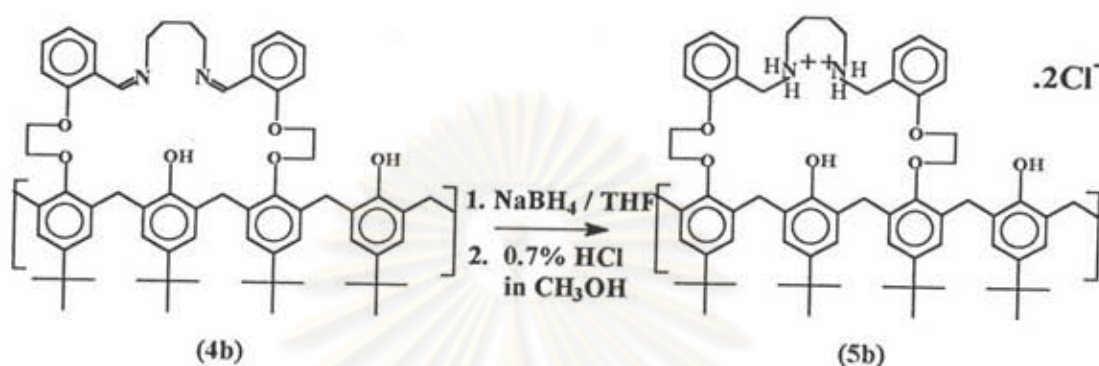
Into a 500 mL 2-necked round bottom flask was added 25, 27-*bis*[2-[(1-formyl-2-phenyl)oxy]ethyl]-*p*-*tert*-butylcalix[4]arene(3) (3.00g, 3.18 mmol) and acetonitrile (250 mL). After complete dissolution of (3), tetraethylene pentamine (0.66 g, 3.50 mmol) in methanol (50 mL) was added dropwise into the solution. The reaction mixture was refluxed under nitrogen atmosphere for 9 h to afford yellow precipitate. The precipitate was filtered and washed with acetonitrile. Yield 0.95 g, (28%). Mp. 253°C. (decomp.).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) spectrum is shown in Figure A.9 and  $^1\text{H-NMR}$  spectral analysis is shown in Table 3.9. Anal. Calcd for  $\text{C}_{70}\text{H}_{95}\text{O}_6\text{N}_5 \cdot \text{CH}_3\text{OH}$ ; C, 75.16%; H, 8.79%; N, 6.17%. Found: C, 75.68%; H, 8.68%; N, 5.89%.

2.1.9 Preparation of 25,27-[2,2'-[(1,7-(2,6-diammonium)heptylene)-2,2'-diphenoxy]diethyl]-*p*-*tert*-butylcalix[4]arene.dichloride (5a) [43]



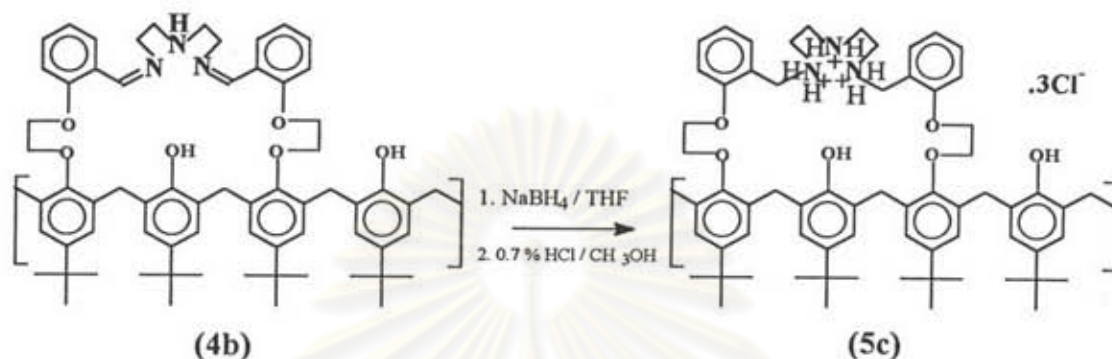
25,27-[2,2'-[1,1'-(1,3-propylenediimino)-2,2'-diphenoxy]diethyl]-*p*-*tert*-butylcalix[4]arene (4a) (2.00 g, 2.04 mmol) was stirred with sodium borohydride (1.17 g, 40.72 mmol) in dried tetrahydrofuran under nitrogen atmosphere for two hours. After the completion of the reaction, the unreacted sodium borohydride was quenched with water. After evaporating to dryness, the solid residue was then extracted with dichloromethane. The organic layer was dried over sodium sulfate and evaporated to dryness. The solid was acidified with a hydrochloric solution in methanol (0.74%v/v) until the pH of the solution reached 1. Upon evaporation of methanol, the product (5a) precipitated as a white solid. Yield : 2.17 g, (95%).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) spectrum is shown in Figure A.10 and  $^1\text{H-NMR}$  analysis is shown in Table 3.10.

2.1.10 Preparation of 25,27-[2,2'-[(1,8-(2,7-diammonium)octylene)-2,2'-diphenoxy]diethyl]-*p*-*tert*-butylcalix[4]arene.dichloride (5b) [43]



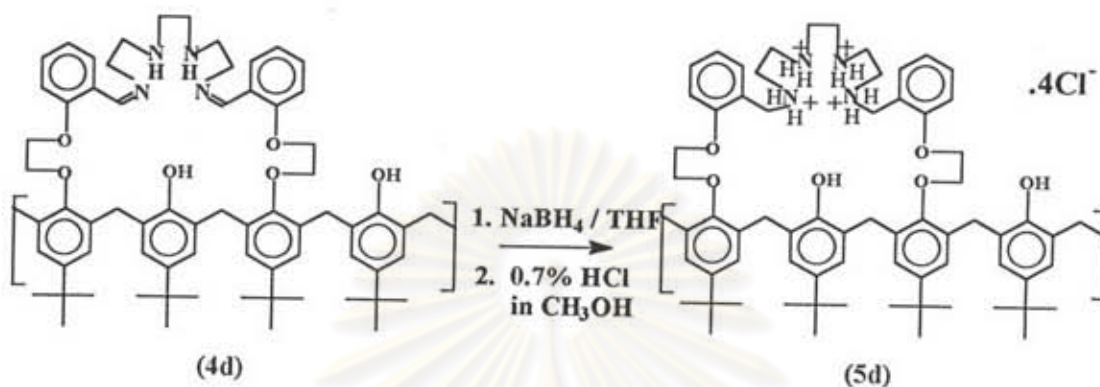
25,27-[2,2'-[1,1'-(1,4-butylenediimino)-2,2'-diphenoxy]diethyl]-*p*-*tert*-butylcalix[4]arene (4c) (2.00 g, 2.00 mmol) was stirred with sodium borohydride (1.56 g, 40.00 mmol) in dried tetrahydrofuran under nitrogen atmosphere for two hours. After the completion of the reaction, the unreacted sodium borohydride was quenched with water. After evaporating to dryness, the solid residue was then extracted with dichloromethane. The organic layer was dried over sodium sulfate and evaporated to dryness. The solid was acidified with a hydrochloric solution in methanol (0.74%v/v) until the pH of the solution reached 1. Upon evaporation of methanol, the product (5b) precipitated as a white solid. Yield: 1.73 g, (81%).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) spectrum is shown in Figure A.11 and  $^1\text{H-NMR}$  analysis is shown in Table 3.11.

2.1.11 Preparation of 25,27-[2,2'-[(1,9-(2,5,8-triammonium)nonyl-ene)-2,2'-diphenoxy]diethyl]-*p*-*tert*-butylcalix[4]arene trichloride (5c)



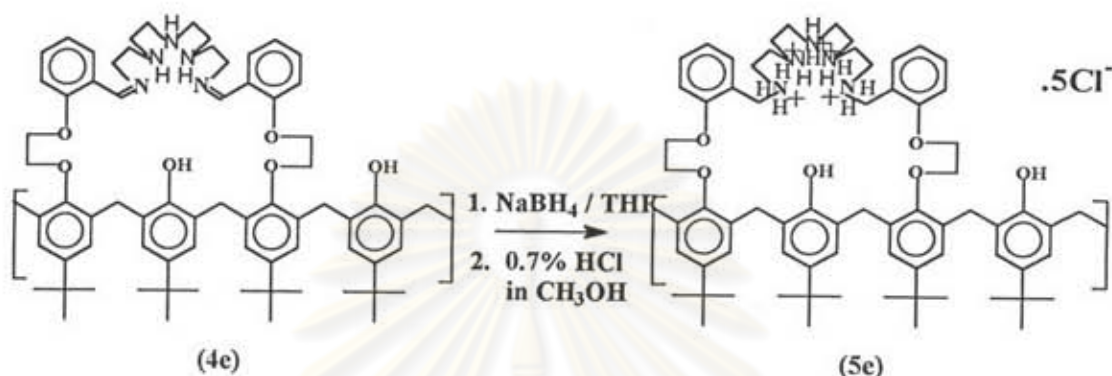
25,27-[2,2'-[(1,1'-(1,5-(3-aza)pentylene)diimino)-2,2'-diphenoxy]diethyl]-*p*-*tert*-butylcalix[4]arene (4d) (6.21 g, 6.14 mmol) was stirred with sodium borohydride (3.49 g, 92.10 mmol) in dried tetrahydrofuran under nitrogen atmosphere for two hours. After the completion of the reaction, the unreacted sodium borohydride was quenched with water. After evaporating to dryness, the solid residue was then extracted with dichloromethane. The organic layer was dried over sodium sulfate and evaporated to dryness. The solid was acidified with a hydrochloric solution in methanol (0.74%v/v) until the pH of the solution reached 1. Upon evaporation of methanol, the product (5c) precipitated as a white solid. Yield : 6.20 g (89%). Mp. 240 °C (decomp.)  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) spectrum is shown in Figure A.12 and  $^1\text{H-NMR}$  analysis is shown in Table 3.12.  $\text{FAB}^+$  mass spectrum is shown in Figure A.22. Anal. Calcd for  $\text{C}_{66}\text{H}_{88}\text{O}_6\text{N}_3\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ ; C, 67.26%; H, 8.04%; N, 3.57%. Found : C, 67.03%; H, 7.54%; N, 3.57%.

2.1.12 Preparation of 25,27-[2,2'-[(1,12-(2,5,8,11-tetraammonium) dodecylene)-2,2'-diphenoxy]diethyl]-*p*-*tert*-butylcalix[4]arene.tetrachloride (5d)



25,27-[2,2'-[(1,1'-(1,9-(3,6-diaza)octylene)diimino)-2,2'-diphenoxy] diethyl]-*p*-*tert*-butylcalix[4]arene (4e) (0.50 g, 0.47 mmol) was stirred with sodium borohydride (0.35 g, 9.50 mmol) in dried tetrahydrofuran under nitrogen atmosphere for two hours. After the completion of the reaction, the unreacted sodium borohydride was quenched with water. After evaporating to dryness, the solid residue was then extracted with dichloromethane. The organic layer was dried over sodium sulfate and evaporated to dryness. The solid was acidified with a hydrochloric solution in methanol (0.74%v/v) until the pH reached 1. Upon evaporation of methanol, the product (5d) precipitated as a yellow solid. Yield : 0.21 g, (37%). Mp. 243 °C. <sup>1</sup>H-NMR (CDCl<sub>3</sub>) spectrum is shown in Figure A.13 and <sup>1</sup>H-NMR analysis is shown in Table 3.13.

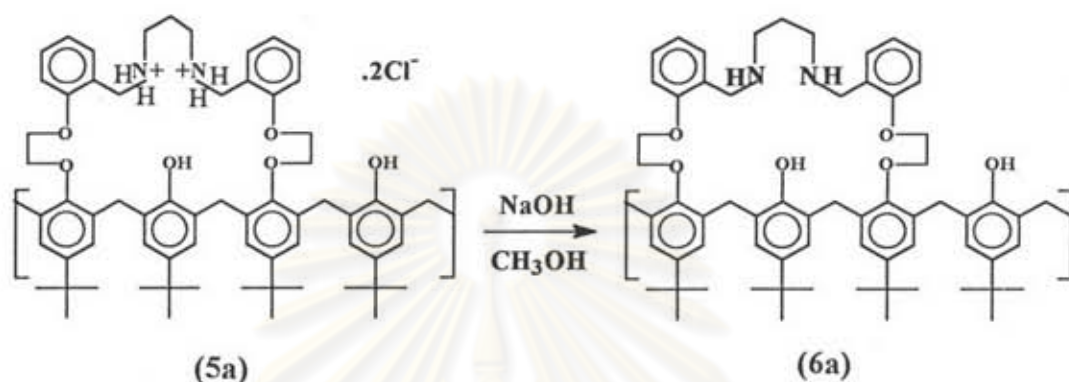
2.1.13 Preparation of 25,27-[2,2'-[(1,15-(2,5,8,11,14-pentaammonium)pentadecylene)-2,2'-diphenoxy]diethyl]-*p*-*tert*-butylcalix[4]arene.pentachloride (5e)



25,27-[2,2'-[(1,1'-[1,11-(3,6,9-triaza)undecylene]diimino)-2,2'-diphenoxy]diethyl]-*p*-*tert*-butylcalix[4]arene (4e) (1.00 g, 0.08 mmol) was stirred with sodium borohydride (0.68 g, 0.69 mmol) in dried tetrahydrofuran under nitrogen atmosphere for two hours. After the completion of the reaction, the unreacted sodium borohydride was quenched with water. After evaporating to dryness, the solid residue was then extracted with dichloromethane. The organic layer was dried over sodium sulfate and evaporated to dryness. The solid was acidified with a hydrochloric solution in methanol (0.74%v/v) until the pH reached 1. Upon evaporation of methanol, the product (5e) precipitated as a yellow solid. Yield: 0.35 g (30%). Mp. 263 °C (decomp.). <sup>1</sup>H-NMR (CDCl<sub>3</sub>) spectrum is shown in Figure A.14 and <sup>1</sup>H-NMR analysis is shown in Table 3.14. Anal. Calcd for C<sub>70</sub>H<sub>104</sub>O<sub>6</sub>N<sub>5</sub>Cl<sub>5</sub>·2H<sub>2</sub>O·3CH<sub>3</sub>OH; C, 61.79%; H, 8.53%; N, 4.94%. Found: C, 61.91%; H, 8.52%; N, 4.60%.



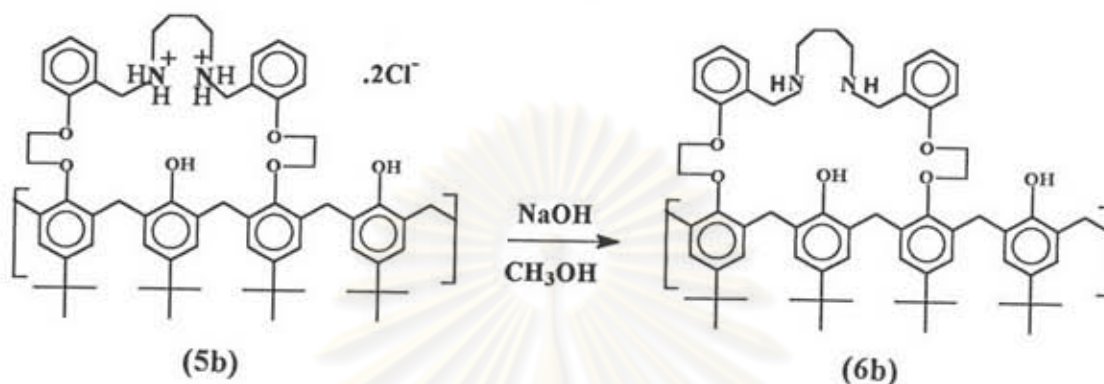
2.1.14 Preparation of 25,27-[2,2'-[(1,7-(2,6-diaza)heptylene)-2,2'-diphenoxy]diethyl]-*p*-*tert*-butylcalix[4]arene (6a) [43]



25,27-[2,2'-[(1,7-(2,6-diammonium)heptylene)-2,2'-diphenoxy]diethyl]-*p*-*tert*-butylcalix[4]arene.dichloride (5a) (4.00 g, 3.78 mmol) was neutralized with sodium hydroxide (0.30 g, 7.55 mmol) in methanol (150 mL). A white precipitate was observed upon a contact of the reactants. The solvent was evaporated to dryness under reduced pressure and the residue was extracted with dichloromethane. After drying over sodium sulfate, (6a) precipitated from the dichloromethane solution by adding methanol. Yield : 3.01 g (80%).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) spectrum is shown in Figure A.15 and  $^1\text{H-NMR}$  analysis is shown in Table 3.15.

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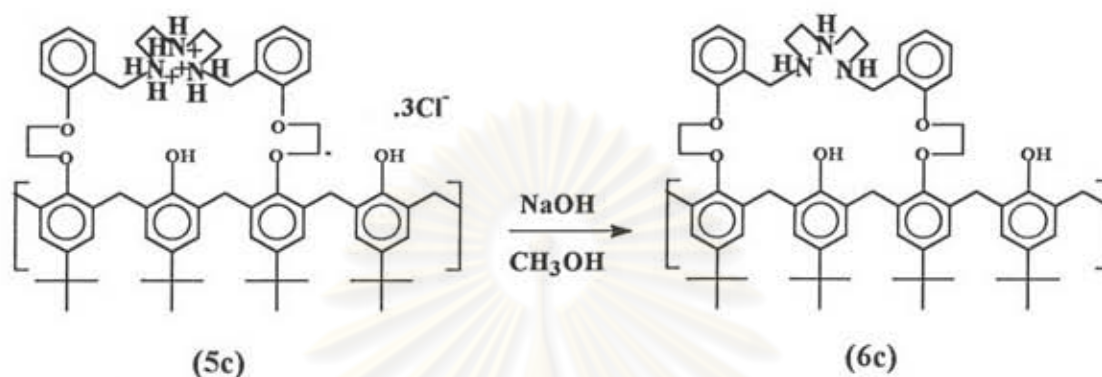
2.1.15 Preparation of 25,27-[2,2'-[(1,8-(2,7-diaza)octylene)-2,2'-diphenoxy]diethyl]-*p*-*tert*-butylcalix[4]arene (6b) [43]



25,27-[2,2'-[(1,8-(2,7-diammonium)octylene)-2,2'-diphenoxy]diethyl]-*p*-*tert*-butylcalix[4]arene.dichloride (5b) (3.00 g, 2.00 mmol) was neutralized with sodium hydroxide (0.16 g, 4.00 mmol) in methanol (50 mL). A white precipitate was observed upon a contact of the reactants. The solvent was evaporated to dryness under reduced pressure and the residue was extracted with dichloromethane. After drying over sodium sulfate, (6b) precipitated from the dichloromethane solution by adding methanol. Yield: 0.98 g, (49%). Mp. 280-281°C (decomp.). <sup>1</sup>H-NMR (CDCl<sub>3</sub>) spectrum is shown in Figure A.16 and <sup>1</sup>H-NMR analysis is shown in Table 3.16.

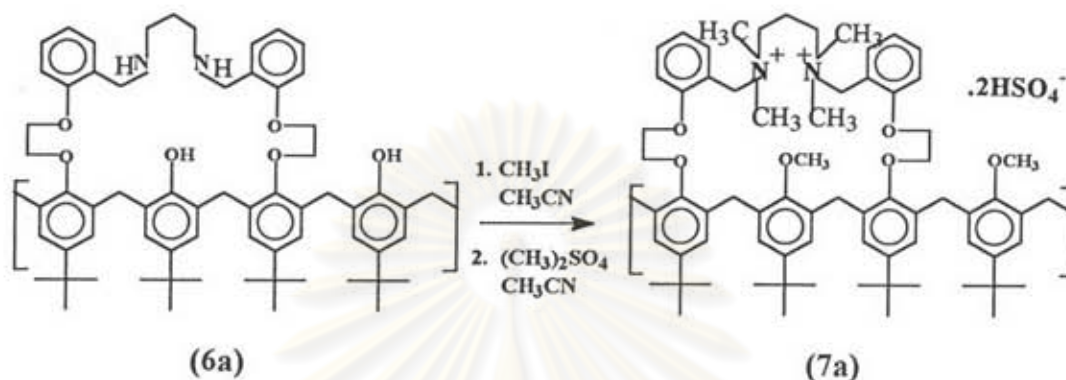
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2.1.16 Preparation of 25,27-[2,2'-[(1,9-(2,5,8-triaza)nonylene)-2,2'-diphenoxy]diethyl]-*p*-*tert*-butylcalix[4]arene (6c)



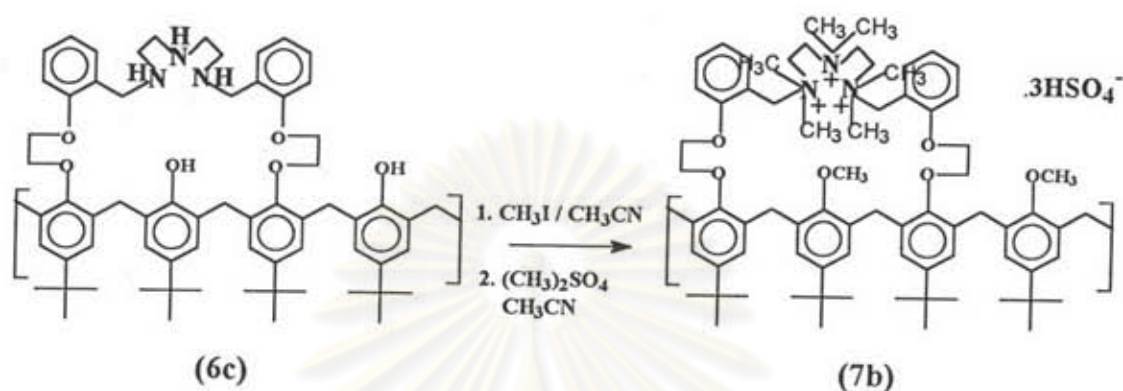
25,27-[2,2'-[(1,9-(2,5,8-triammonium)nonylene)-2,2'-diphenoxy]diethyl]-*p*-*tert*-butylcalix[4]arene.trichloride (5c) (3.00 g, 2.66 mmol) was neutralized with sodium hydroxide (0.32 g, 8.00 mmol) in methanol (120 mL). A white precipitate was observed upon a contact of the reactants. The solvent was evaporated to dryness under reduced pressure and the residue was extracted with dichloromethane. After drying over sodium sulfate, (6c) precipitated from the dichloromethane solution by adding methanol. Yield : 2.40 g, (89%). Mp. 249-250 °C (decomp.).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) is shown in Figure A.17 and  $^1\text{H-NMR}$  analysis is shown in Table 3.17. Mass spectrum ( $\text{FAB}^+$ ) 1016.4 (100%) is shown in Figure A.23. Anal. Calcd for  $\text{C}_{66}\text{H}_{85}\text{O}_6\text{N}_3$ ; C, 77.98%; H, 8.43%; N, 4.14%. Found : C, 77.78%; H, 8.08%; N, 4.56%.

**2.1.17 Preparation of 24,26-dimethyl-25,27-[2,2'-[(1,7-(2,6-dimethylammonium)heptylene)-2,2'-diphenoxy]diethyl]-*p*-*tert*-butylcalix[4]arene di(hydrogensulfate) (7a) [44]**



25,27-[2,2'-[(1,7-(2,6-diaza)heptylene)-2,2'-diphenoxy]diethyl]-*p*-*tert*-butylcalix[4]arene (6a) (3.00 g, 3.03 mmol), and acetonitrile (250 mL) were put in a 500 mL 2-necked round bottom flask. After completed dissolution potassium carbonate (5.50 g, 40.00 mmol) and methyl iodide (3.0 mL, 34.5 mmol) were added into the solution. The reaction mixture was refluxed under nitrogen atmosphere for 21 hours. The reaction mixture was filtered and the filtrate was evaporated to dryness. The filtrate residue was put in a new round bottom flask and dissolved with acetonitrile (250 mL). Dimethylsulfate (0.70 mL, 7.30 mmol) was added into the solution. The reaction mixture was refluxed under nitrogen atmosphere for 5 hours. A white precipitate of (7a) was filtered. Yield: 2.10 g, (82%).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) spectrum is shown in Figure A.18 and  $^1\text{H-NMR}$  analysis is shown in Table 3.18.

2.1.18 Preparation of 24,26-dimethyl-25,27-[2,2'-[(1,9-(2,5,8-trimethylammonium)nonylene)-2,2'-diphenoxy]diethyl]-*p*-*tert*-butylcalix[4]arene tri(hydrogensulfate) (7b)



25,27-[2,2'-[(1,9-(2,5,8-trimethylammonium)nonylene)-2,2'-diphenoxy]diethyl]-*p*-*tert*-butylcalix[4]arene (6c) (3.50 g, 3.45 mmol), methyl iodide (3.0 mL, 34.5 mmol), potassium carbonate (5.50 g, 40.00 mmol) and acetonitrile (250 mL) were put in a 500 mL 2-necked round bottom flask and the reaction mixture was refluxed under nitrogen atmosphere for 21 hours. This reaction was filtered and the filtrate was evaporated to dryness. The filtrate residue was put in a new round bottom flask and dissolved with acetonitrile (250 mL). Dimethylsulfate (0.70 mL, 7.30 mmol) was added into the solution. The reaction mixture was refluxed under nitrogen atmosphere for 5 hours. A white precipitate of (7b) was filtered. Yield: 2.46 g, (54%). Mp. 232 °C (decomp).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) spectrum is shown in Figure A.19 and  $^1\text{H-NMR}$  analysis is shown in Table 3.19. Mass spectrum ( $\text{FAB}^+$ ) is shown in Figure A.24.

## 2.2 Complexation Study

### Chemicals

1. 25,27-[2,2'-[(1,9-(2,5,8-triammonium)nonylene)-2,2'-diphenoxy]diethyl]-*p-tert*-butylcalix[4]arene.trichloride (5c)
2. 24,26-dimethyl-25,27-[2,2'-[(1,7-(2,6-tetramethylammonium)heptylene)-2,2'-diphenoxy]diethyl]-*p-tert*-butylcalix[4]arene.di(hydrogensulfate) (7a)
3. 24,26-dimethyl-25,27-[2,2'-[(1,9-(2,5,8-hexamethylammonium)nonylene)-2,2'-diphenoxy]diethyl]-*p-tert*-butylcalix[4]arene.tri(hydrogensulfate) (7b)
4. Dichloromethane (Analar grade, J.T. Baker, USA.)
5. Methanol (Analar grade, J.T. Baker, USA.)
5. Sodium carbonate anhydrous (Analar grade, Fluka, Switzerland)
6. Sodium nitrate (Analar grade, Fluka, Switzerland)

### Apparatus

1. Balance (Satorius) ( $\pm 0.0000$  g)
2. Fourier Transform NMR Spectrometer ACF 200 MHz, Bruker, Switzerland
3. Fourier Transform NMR Spectrometer 500 MHz, Jeol, Japan
4. Eyela Magnetic Stirrer RC-2, Eyela, Japan

## Procedure

### 2.2.1 Complexation study between sodium nitrate and ligand (5c)

Ligand (5c) (0.0250 g, 0.0223 mmol) was dissolved in dichloromethane (5 mL). After complete dissolution of (5c), various sodium nitrate amounts were added in the solution, to have anion : ligand ratios from 0.0 : 1.0 to 4.0 : 1.0 (Table 2.2.1). The reaction mixture was stirred for 36 hours and filtered. The filtrate was evaporated to dryness and the solid was dissolved in deuterated chloroform for  $^1\text{H-NMR}$  spectral study.  $^1\text{H-NMR}$  spectra are shown in Figures A.27-A.35.

Table 2.2.1 Ratios of sodium nitrate to ligand (5c) in dichloromethane (A = anion,  $\text{NO}_3^-$ )

Mole ratio (A:L)	Sodium nitrate (g)	Ligand (5c) (g)	Dichloromethane (mL)
0.0 : 1.0	0.0000	0.0250	5.00
0.5 : 1.0	0.0008	0.0250	5.00
1.0 : 1.0	0.0015	0.0250	5.00
1.5 : 1.0	0.0019	0.0250	5.00
2.0 : 1.0	0.0027	0.0250	5.00
2.5 : 1.0	0.0030	0.0250	5.00
3.0 : 1.0	0.0038	0.0250	5.00
3.5 : 1.0	0.0057	0.0250	5.00
4.0 : 1.0	0.0076	0.0250	5.00

### 2.2.2 Complexation study between sodium carbonate and ligand (5c)

Ligand (5c) (0.0250 g, 0.0223 mmol) was dissolved in dichloromethane (10 mL). After complete dissolution of (5c), various sodium carbonate amounts were added in the solution, to have anion : ligand ratios from 0.0 : 1.0 to 4.0 : 1.0 (Table 2.2.2). The reaction mixture was stirred for 36 hours and filtered. The filtrate was evaporated to dryness and the solid was dissolved in deuterated chloroform for  $^1\text{H-NMR}$  spectral study.  $^1\text{H-NMR}$  spectra are shown in Figures A.38-A.46

**Table 2.2.2** Ratios of sodium carbonate to ligand (5c) in dichloromethane  
(A = anion,  $\text{CO}_3^{2-}$ )

Mole ratio (A:L)	Sodium carbonate (g)	Ligand (5c) (g)	Dichloromethane (mL)
0.0 : 1.0	0.0000	0.0250	10.00
0.5 : 1.0	0.0012	0.0250	10.00
1.0 : 1.0	0.0024	0.0250	10.00
1.5 : 1.0	0.0036	0.0250	10.00
2.0 : 1.0	0.0048	0.0250	10.00
2.5 : 1.0	0.0060	0.0250	10.00
3.0 : 1.0	0.0072	0.0250	10.00
3.5 : 1.0	0.0084	0.0250	10.00
4.0 : 1.0	0.0096	0.0250	10.00



### 2.2.3 Competitive complexation study between sodium carbonate and sodium nitrate with ligand (5c)

2.2.3.1 Ligand (5c) (0.1500 g, 0.1330 mmol) was dissolved in dichloromethane (10 mL). After complete dissolution of (5c), sodium nitrate 0.1130 g, 0.1330 mmol ( $A : L = 1:1$ ) was added in the solution. The reaction mixture was stirred for 36 hours and filtered. The filtrate was evaporated to dryness and the solid was dissolved in deuterated chloroform for  $^1\text{H-NMR}$  spectral study.  $^1\text{H-NMR}$  spectrum is shown in Figure A.47. The filtrate was evaporated to dryness and the solid was put in 10 mL dichloromethane and reacted with sodium carbonate (0.0141 g, 0.1330 mmol) upon stirring for 36 hours. The unreacted sodium carbonate was filtered. The filtrate was evaporated to dryness and the solid was dissolved in deuterated chloroform for  $^1\text{H-NMR}$  spectral study.  $^1\text{H-NMR}$  spectrum is shown in Figure A.48.

2.2.3.2 Ligand (5c) (0.1500 g, 0.1330 mmol) was dissolved in dichloromethane (10 mL). After complete dissolution of (5c), sodium carbonate (0.0141 g, 0.1330 mmol) and sodium nitrate (0.1130 g, 0.1330 mmol) were added in the solution,  $A_1 : L : A_2 = 1 : 1 : 1$ . The reaction mixture was stirred for 36 hours and filtered. The filtrate was evaporated to dryness and the solid was dissolved in deuterated chloroform for  $^1\text{H-NMR}$  spectral study.  $^1\text{H-NMR}$  spectrum is shown in Figure 49.

#### 2.2.4 Complexation study between sodium nitrate and ligand (7a)

Ligand (7a) (0.0500 g, 0.0035 mmol) was dissolved in methanol (10 mL). After completed dissolution of (7a), sodium nitrate was added in the solution, to have anion : ligand mole ratios 0.0, 1.0 and 4.0 (Table 2.2.4). The reaction mixture was stirred for 36 hours and filtered. The filtrate was evaporated to dryness and the solid was dissolved in deuterated chloroform for  $^1\text{H-NMR}$  spectral study.  $^1\text{H-NMR}$  spectrum are shown in Figures A.50-A.52.

Table 2.2.4 Ratios of sodium nitrate to ligand (7a) in methanol  
(A = anion,  $\text{NO}_3^-$ )

Mole ratio (A : L)	Sodium nitrate (g)	Ligand (7a) (g)	Methanol (mL)
0.0 : 1.0	0.0000	0.0500	10.00
1.0 : 1.0	0.0030	0.0500	10.00
4.0 : 1.0	0.0119	0.0500	10.00

#### 2.2.5 Complexation study between sodium carbonate and ligand (7a)

Ligand (7a) (0.0500 g, 0.0035 mmol) was dissolved in methanol (10 mL). After completed dissolution of (7a), sodium carbonate was added in the solution, to have anion : ligand mole ratios 1.0 and 4.0 (Table 2.2.5). The reaction mixture was stirred for 36 hours and filtered. The filtrate was evaporated to dryness and the solid was dissolved in deuterated chloroform for  $^1\text{H-NMR}$  spectral study.  $^1\text{H-NMR}$  spectrum are shown in Figures A.53-A.54.

**Table 2.2.5** Ratios of sodium carbonate to ligand (7a) in methanol  
(A = anion,  $\text{CO}_3^{2-}$ )

Mole ratio (A : L)	Sodium carbonate (g)	Ligand (7a) (g)	Methanol (mL)
1.0 : 1.0	0.0037	0.0500	10.00
4.0 : 1.0	0.0142	0.0500	10.00

### 2.2.6 Complexation study between sodium nitrate and ligand (7b)

Ligand (7b) (0.0500 g, 0.0351 mmol) was dissolved in dichloromethane (10 mL). After completed dissolution of (7b), sodium nitrate was added in the solution, to have anion : ligand mole ratios 0.0, 1.0 and 4.0 (Table 2.2.6). The reaction mixture was stirred for 36 hours and filtered. The filtrate was evaporated to dryness and the solid was dissolved in deuterated chloroform for  $^1\text{H-NMR}$  spectral study.  $^1\text{H-NMR}$  spectrum are shown in Figures A.55-A.57.

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**Table 2.2.6** Ratios of sodium nitrate to ligand (7b) in dichloromethane  
(A = anion,  $\text{NO}_3^-$ )

Mole ratio (A : L)	Sodium nitrate (g)	Ligand (7b) (g)	Dichloromethane (mL)
0.0 : 1.0	0.0000	0.0500	10.00
1.0 : 1.0	0.0032	0.0500	10.00
4.0 : 1.0	0.0128	0.0500	10.00

### 2.2.7 Complexation study between sodium carbonate and ligand (7b)

Ligand (7b) (0.0500 g, 0.0351 mmol) was dissolved in dichloromethane (10 mL). After completed dissolution of (7b), sodium carbonate was added in the solution, to have anion : ligand mole ratios 0.0, 1.0 and 4.0 (Table 2.2.7). The reaction mixture was stirred for 36 hours and filtered. The filtrate was evaporated to dryness and the solid was dissolved in deuterated chloroform for  $^1\text{H-NMR}$  spectral study.  $^1\text{H-NMR}$  spectrum are shown in Figures A.58-A.59.

**Table 2.2.7** Ratios of sodium carbonate to ligand (7b) in dichloromethane  
(A = anion,  $\text{CO}_3^{2-}$ )

Mole ratio (A : L)	Sodium carbonate (g)	Ligand (7b) (g)	Dichloromethane (mL)
1.0 : 1.0	0.0040	0.0500	10.00
4.0 : 1.0	0.0159	0.0500	10.00