CHAPTER III

EXPERIMENT

3.1 Synthesis of Calix[4]arene Derivatives

3.1.1 General

All reactions were carried out under nitrogen atmosphere unless otherwise noted. Analytical thin-layer chromatography (TLC) was performed with silica gel 60 F_{254} aluminium-backed sheet (MERCK). Visualization was accomplished *via* iodine vapor or UV light. Liquid chromatography was performed by using 70-230 mesh silica gel.

3.1.2 Materials

All materials were standard reagents and used without further purification unless otherwise noted. The solvents were used as received from commercial sources. All reagents were purchased from Merck and Fluka Chemical Companies. The dithia diamine compounds, 3,7-dithianonane-1,9-diamine and 3,6-dithiaoctane-1,9-diamine, were prepared according to published procedures[26,27].

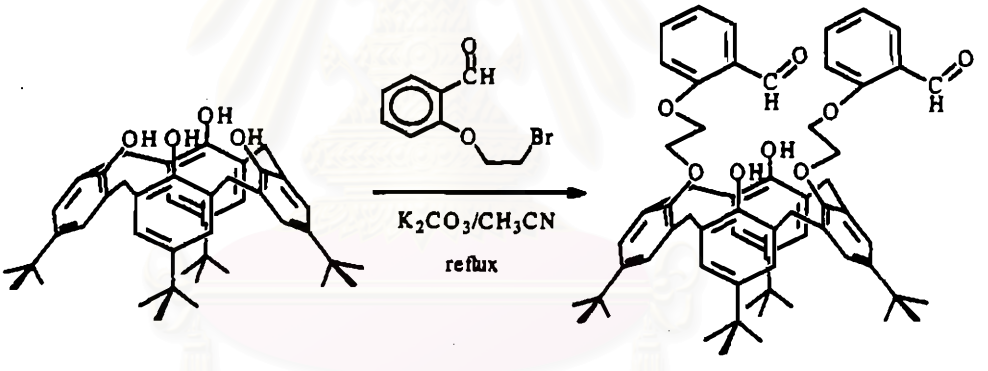
3.1.3 Analytical Procedures

The ^{1}H-NMR spectra were recorded at 200 MHz on a Bruker ACF200. The IR spectra were obtained on a Nicolet Impact 410 FTIR spectrophotometer. Mass

spectra were registered on a FAB mass spectrometer at Chulabhon Research Institute. Elemental analysis were carried out on a Perkin Elmer Elemental Analyzer 2400 CHN at the Scientific and Technological Research Equipment Center of Chulalongkorn University. Potentiometric titrations were carried out on a Mettler DL 25 automatic titrator equipped with a Mettler DG 113-SC combined pH electrode. Temperature was controlled at 25 °C during titration by Heto DT-2 thermostat.

3.1.4 Synthetic Procedures

(a) Preparation of 25,27-((2,2′-diethoxy)benzaldehyde)-*p-tert*-butylcalix[4]arene, 1.

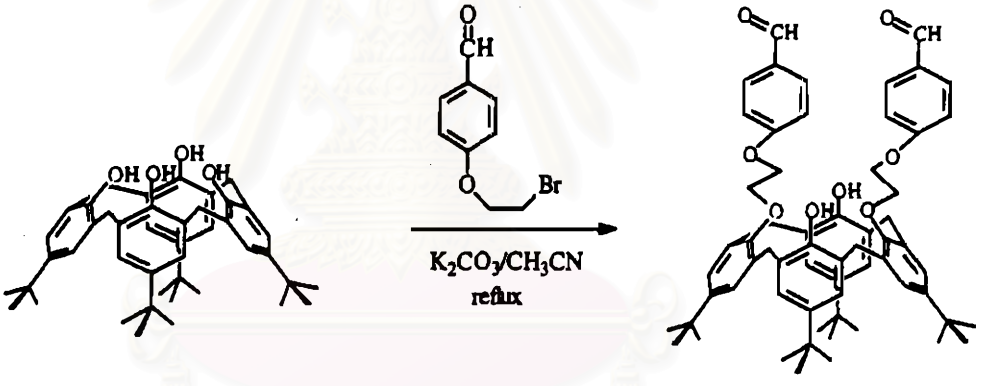


1

Into a 1 L 2-necked round bottom flask containing *p-tert*-butylcalix[4] arene (11.70 g, 18.1 mmol), K_2CO_3 (20.00 g, 145.6 mmol) and acetonitrile (350 mL) was added dropwise a solution of 2-(2′-bromoethoxy)benzaldehyde (9.53 g, 41.7 mmol) in acetonitrile (150 mL). The reaction was stirred and heated at reflux under nitrogen for 63 h. The solution was allowed to cool down. K_2CO_3 was filtered off and washed with a large amount of acetone and dichloromethane. White solid precipitated upon removal of solvent and addition of methanol. The solid was then placed on a silica gel column with dichloromethane as an eluant. The compound **1** was obtained

as white solid. Yield : 12.18 g (71%). ^{1}H-NMR ($CDCl_3$) (Figure A.1) 10.51 (2H, s, C*H*O), 7.86 (2H, d, *J* (HH) 7.66 Hz, H_A), 7.56-7.47 (2H, m, H_B), 7.54 (2H, s, ArO*H*), 7.06-6.96 (4H, m, H_C and H_D), 7.02 (4H, s, HOAr*H*), 6.88 (4H, s, ROAr*H*), 4.42-4.40 (8H, m, OCH_2CH_2O), 4.21 and 3.31 (AB system, 8H, *J* (HH) 13.6 Hz, $ArCH_AH_BAr$), 1.26 (18H, s, HOAr-*t*-C_4H_9), 1.03 (18H, s, ROAr-*t*-C_4H_9). IR spectrum (KBr pellet) (Figure A.2) 1685 cm^{-1} (>C=O group). FAB m/z 944.5 (M^+). Anal. Calcd. for $C_{62}H_{72}O_8.CH_3OH$: C, 77.42 ; H, 7.83. Found : C, 77.54 ; H, 7.79.

(b) Preparation of 25,27-((4,4′-diethoxy)benzaldehyde)-*p-tert*-butylcalix[4]arene, 2.

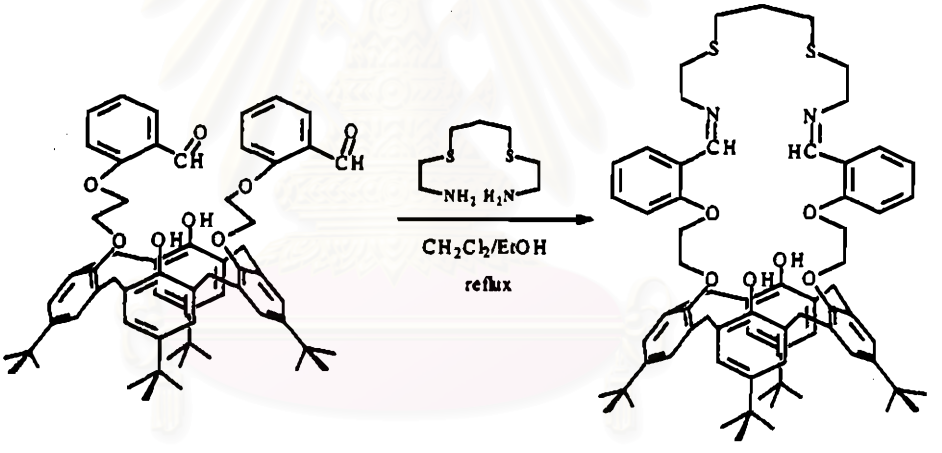


2

Into a 1 L 2-necked round bottom flask containing *p-tert*-butylcalix[4] arene (11.70 g, 18.1 mmol), K_2CO_3 (20.00 g, 145.6 mmol) and acetonitrile (350 mL) was added dropwise a solution of 4-(2′-bromoethoxy)benzaldehyde (9.53 g, 41.7 mmol) in acetonitrile (100 mL). The reaction was stirred and heated at reflux under nitrogen for 53 h. The solution was allowed to cool down. K_2CO_3 was filtered off and washed with a large amount of acetone and dichloromethane. The filtrate was concentrated on a rotary evaporator to yield a creamy caramel-like residue. The residue was then placed on a silica gel column with 2% acetone in dichloromethane as

an eluant. The compound **2** was obtained as white solid. Yield : 9.16 g (54%). ^{1}H-NMR ($CDCl_3$) (Figure A.3) 9.90 (2H, s, C*H*O), 7.85 (4H, d, *J* (HH) 8.8 Hz, ArH_AH_B), 7.03 (4H, d, *J* (HH) 8.8 Hz ArH_AH_B), 7.35 (2H, s, ArO*H*), 7.06 (4H, s, HOAr*H*), 6.87 (H, s, ROAr*H*), 4.37 and 3.33 (8H, dd, *J* (HH) 13.1 Hz, ArCH_AH_BAr), 4.33 (8H, s, OCH_2CH_2O), 1.29 (18H, s, HOAr-*t*-C$_4H_9$), 1.03 (18H, s, ROAr-*t*-C$_4H_9$). IR spectrum (KBr pellet)(Figure A.4) 1695 cm^{-1} (>C=O group). FAB m/z 944.2 (M^+). Anal. Calcd. For $C_{62}H_{72}O_8$: C, 78.77 ; H, 7.66. Found : C, 78.25 ; H, 8.05.

(c) Preparation of 25,27-((2,2′-diethoxy)benzyl)-3,7-dithianonane-1,9-diimine-*p*-*tert*-butylcalix[4]arene, 3.

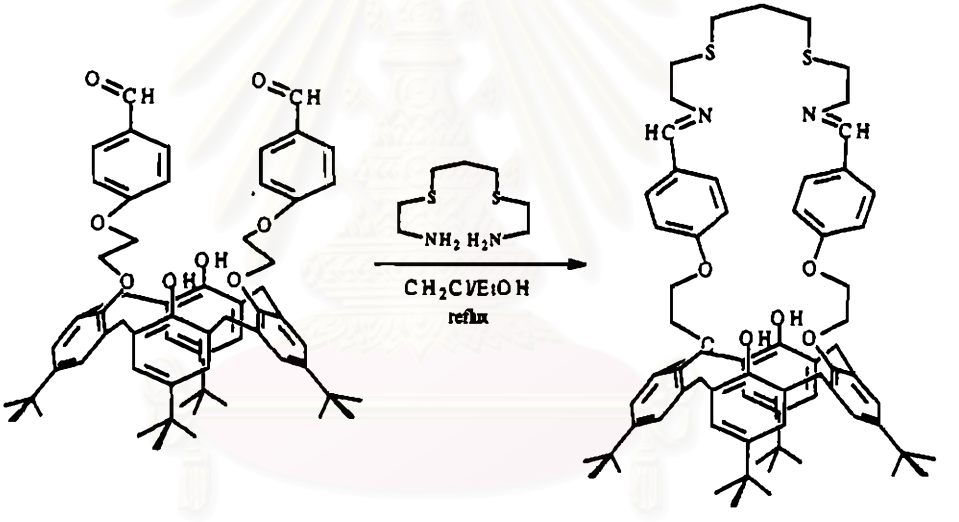


1 **3**

The compound **1** (2.03 g, 2.2 mmol), dichloromethane (20 mL) and ethanol (200 mL) were placed into a 2-necked round bottom flask. An ethanolic solution (30 mL) of 1,9-diaza-3,7-dithianonane (0.49 g, 2.6 mmol) 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 : 2.02 g (85 %). ^{1}H-NMR ($CDCl_3$) (Figure A.5) 8.82 (2H, s, C*H*=N), 7.94-6.91 (8H, m, Ar$H_AH_BH_CH_D$), 7.40 (2H, s, ArO*H*), 7.03 (4H, s,

HOAr*H*), 6.84 (4H, s, ROAr*H*), 4.32 and 3.37 (8H, dd, *J* (HH) 12.9 Hz, ArCH_AH_BAr), 4.38 (8H, s, OCH_2CH_2O), 3.54 (4H, t, NCH_2CH_2S), 2.59 (4H, t, NCH_2CH_2S), 2.48 (4H, t, SCH_2CH$_2$CH_2S), 1.69 (2H, q, SCH$_2$CH_2CH$_2$S), 1.30 (18H, s, HOAr-*t*-C$_4H_9$), 0.98 (18H, s, ROAr-*t*-C$_4H_9$). IR spectrum (KBr pellet)(Figure A.6) 1634 cm^{-1} (>C=N- group). FAB m/z 1103.1 (M^+). Anal. Calcd. For $C_{69}H_{86}O_6N_2S_2$: C, 75.10 ; H, 7.85 ; N, 2.54. Found : C, 75.07 ; H, 7.86 ; N, 2.62.

(d) Preparation of 25,27-((4,4′-diethoxy)benzyl)-3,7-dithianonane-1,9-diimine-*p*-*tert*-butylcalix[4]arene, 4.

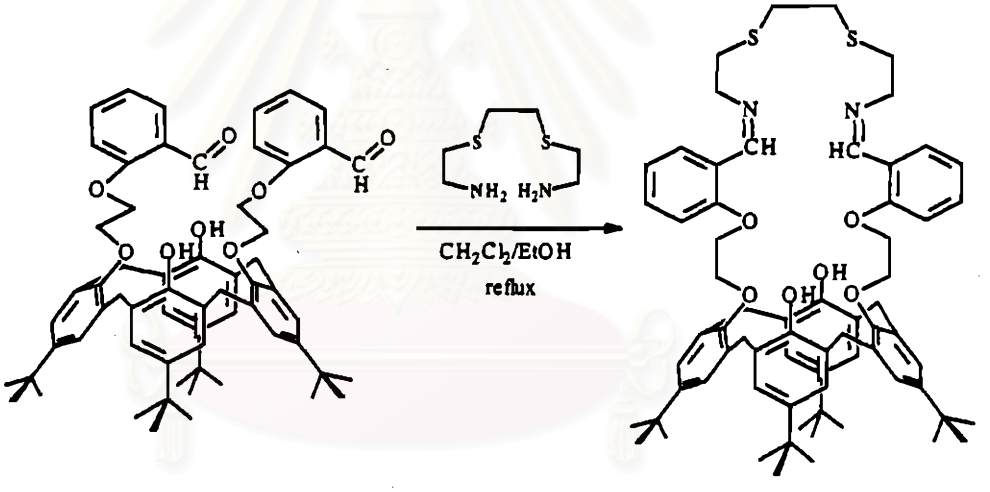


2 4

The compound **2** (1.07 g, 1.1 mmol), dichloromethane (20 mL) and ethanol (200 mL) were placed into a 2-necked round bottom flask. An ethanolic solution (30 mL) of 1,9-diaza-3,7-dithianonane (0.24 g, 1.2 mmol) 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 : 0.84 g (71 %). ^{1}H-NMR ($CDCl_3$) (Figure A.7) 8.19 (2H, s, C*H*=N), 7.62 (4H, d, *J* (HH) 8.8 Hz, ArH_AH_B), 6.90 (4H, d, *J* (HH) 8.8 Hz,

ArH_AH_B), 7.33 (2H, s, ArO*H*), 7.01 (4H, s, HOAr*H*), 6.82 (4H, s, ROAr*H*), 4.36 and 3.27 (8H, dd, *J* (HH) 12.8 Hz, ArCH_AH_BAr), 4.29 (8H, s, OCH_2CH_2O), 3.75 (4H, t, NCH_2CH_2S), 2.81 (4H, t, NCH_2CH_2S), 2.64 (4H, t, SCH_2CH$_2$CH_2S), 1.87 (2H, q, SCH$_2$CH_2CH$_2$S), 1.25 (18H, s, HOAr-*t*-C$_4H_9$), 0.98 (18H, s, ROAr-*t*-C$_4H_9$). IR spectrum (KBr pellet)(Figure A.8) 1642 cm^{-1} (>C=N- group). FAB m/z 1102.9 (M^+). Anal. Calcd. For $C_{69}H_{86}O_6N_2S_2$: C, 75.10 ; H, 7.85 ; N, 2.54. Found : C, 75.54 ; H, 7.82 ; N, 2.48.

(e) Preparation of 25,27-((2,2′-diethoxy)benzyl)-3,6-dithiaoctane-1,8-diimine-*p*-*tert*-butylcalix[4]arene, 5.

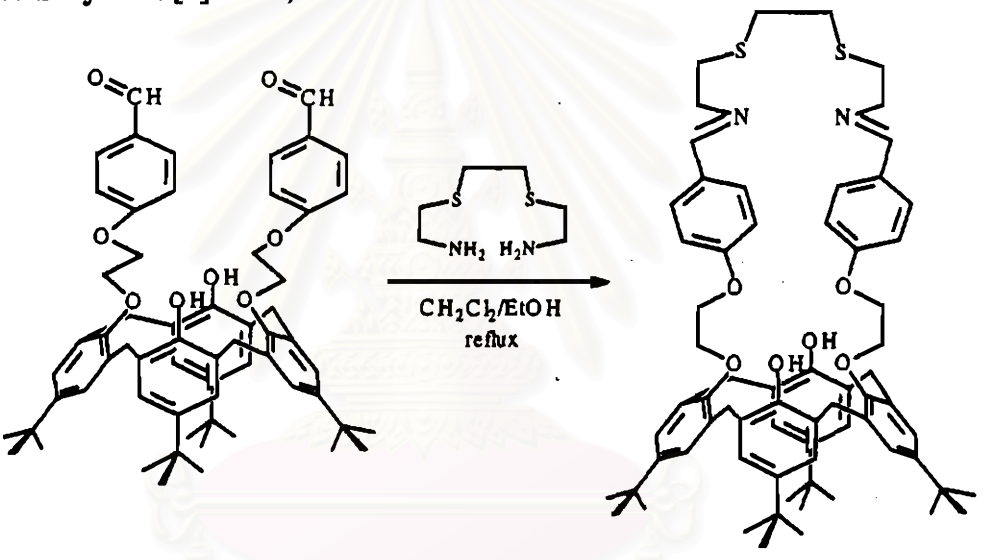


1 **5**

The compound **1** (1.03 g, 1.1 mmol), dichloromethane (20 ml) and ethanol (200 mL) were placed in a 2-necked round bottom flask. An ethanolic solution (30 mL) of 1,8-diaza-3,6-dithiaoctane (0.23 g, 1.3 mmol) 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 : 0.51 g (43 %). ^{1}H-NMR ($CDCl_3$) (Figure A.9) 8.81 (2H, s, C*H*=N), 7.91-6.81 (8H, m, Ar$H_AH_BH_CH_D$), 7.31 (2H, s, ArO*H*), 7.04 (4H, s, HOAr*H*), 6.84 (4H, s,

ROAr*H*), 4.32 and 3.34 (8H, dd, *J* (HH) 13.3 Hz, ArCH_AH_BAr), 4.38 (8H, s, OCH_2CH_2O), 3.51 (4H, t, NCH_2CH_2S), 2.57 (4H, t, NCH_2CH_2S), 2.50 (4H, s, SCH_2CH_2S), 1.26 (18H, s, HOAr-*t*-C_4H_9), 0.96 (18H, s, ROAr-*t*-C_4H_9). IR spectrum (KBr pellet)(Figure A.10) 1634 cm^{-1} (>C=N- group). Anal. Calcd. For $C_{68}H_{84}O_6N_2S_2$: C, 74.96 ; H, 7.77 ; N, 2.57. Found : C, 74.24 ; H, 7.96 ; N, 2.46.

(f) Preparation of 25,27-((4,4′-diethoxy)benzyl)-3,6-dithiaoctane-1,8-diimine-*p*-*tert*-butylcalix[4]arene, 6.

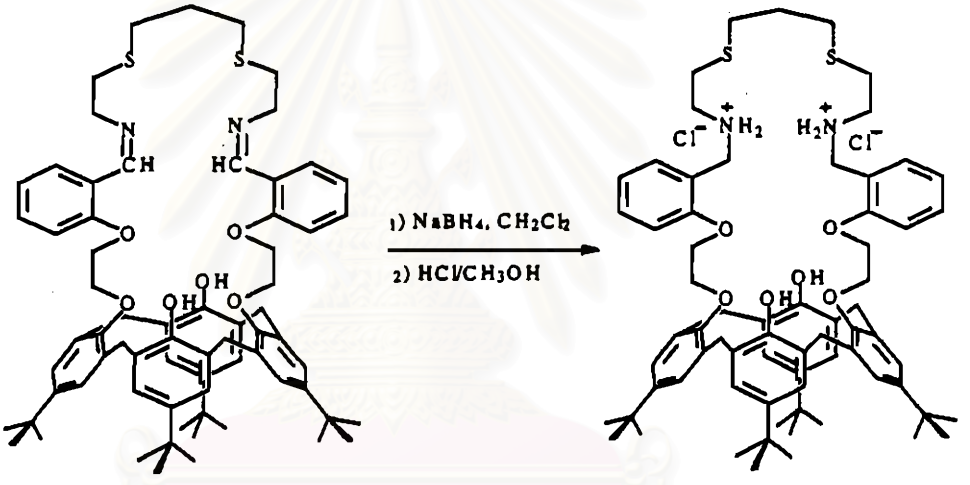


2 **6**

The compound **2** (0.97 g, 1.0 mmol), dichloromethane (20 ml) and ethanol (200 ml) were placed in a 2-necked round bottom flask. An ethanolic solution (30 mL) of 1,8-diaza-3,6-dithiaoctane (0.25 g, 1.4 mmol) 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 : 0.45 g (40 %). ^{1}H-NMR ($CDCl_3$) (Figure A.11) 8.17 (2H, s, C*H*=N), 7.65 (4H, d, *J* (HH) 8.8 Hz, ArH_AH_B), 6.91 (4H, d, *J* (HH) 8.2 Hz, ArH_AH_B), 7.31 (2H, s, ArO*H*), 7.03 (4H, s, HOAr*H*), 6.8 (4H, s, ROAr*H*), 4.33 and 3.30 (8H, dd, *J* (HH)

13.0 Hz, ArCH_AH_BAr), 4.26 (8H, s, OCH_2CH_2O), 3.77 (4H, t, NCH_2CH_2S), 2.86 (4H, t, NCH_2CH_2S), 2.79 (4H, t, SCH_2CH_2S), 1.25 (18H, s, HOAr-*t*-C_4H_9), 1.05 (18H, s, ROAr-*t*-C_4H_9). IR spectrum (KBr pellet)(Figure A.12) 1641 cm^{-1} (>C=N- group). Anal. Calcd. For $C_{69}H_{86}O_6N_2S_2$: C, 74.96 ; H, 7.77 ; N, 2.57. Found : C, 73.33 ; H, 7.46 ; N, 2.22.

(g) Preparation of 25,27-((2,2′-diethoxy)benzyl)-3,7-dithianonane-1,9-diimine-*p*-*tert*-butylcalix[4]arene dihydrogenchloride, 7.

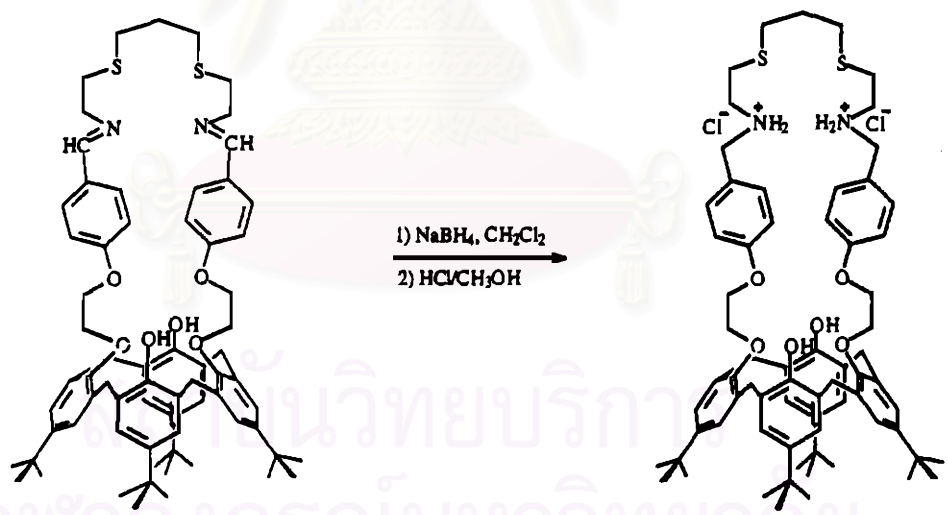


3 7

Into a solution of **3** (0.94 g, 0.9 mmol) in dichloromethane (100 ml) was added with sodium $NaBH_4$ (0.67 g, 17.7 mmol). The mixture was stirred under nitrogen atmosphere for 24 h at room temperature. Water was then added to quench excess $NaBH_4$. The organic layer was extracted with several portions of water until the pH of aqueous phase reached 7. The combined organic layers were dried over sodium sulfate anhydrous, filtered and evaporated to dryness to obtain white solid. A solution of HCl/CH_3OH (0.74 % V/V) was slowly added to dissolve the white solid. The addition was continued until the pH of the solution reached 1. Upon slowly

evaporation of methanol, the product precipitated as white crystals. Yield : 0.65 g (65%). ^{1}H-NMR ($CDCl_3$) (Figure A.13) 9.71 (4H, broad, $ArCH_2NH_2^+$), 7.78 (2H, s, ArO*H*), 7.38-6.88 (8H, m, $ArH_AH_BH_CH_D$), 6.94 (4H, s, HOAr*H*), 6.85 (4H, s, ROAr*H*), 4.97 and 4.43 (12H, broad, OCH_2CH_2O and $ArCH_2N^+$), 4.29 and 3.19 (AB system, 8H, *J* (HH) 12.9 Hz, $ArCH_AH_BAr$), 3.14 (8H, broad, NCH_2CH_2S and NCH_2CH_2S, 2.60 (4H, broad, $SCH_2CH_2CH_2S$), 1.99 (2H, broad, $SCH_2CH_2CH_2S$), 1.20 (18H, s, HOAr-*t*-C_4H_9), 0.99 (18H, s, ROAr-*t*-C_4H_9). FAB m/z 1107.8 (M^+). Anal. Calcd. For $C_{69}H_{92}O_6N_2S_2Cl_2$: C, 70.20 ; H, 7.86 ; N, 2.37. Found : C, 70.18 ; H, 7.70 ; N, 2.30.

(h) Preparation of 25,27-((4,4′-diethoxy)benzyl)-3,7-dithianonane-1,9-diimine-*p*-*tert*-butylcalix[4]arene dihydrogenchloride, 8.



4 8

Into a solution of **4** (1.09 g, 1.0 mmol) in dichloromethane (100 ml) was added $NaBH_4$ (0.83 g, 22.0 mmol). The mixture was stirred under nitrogen atmosphere for 24 h at room temperature. Water was then added to quench excess $NaBH_4$. The organic layer was extracted with several portions of water until the pH of the aqueous

phase reached 7. The combined organic layers were later dried over sodium sulfate anhydrous, filtered and evaporated to dryness to obtain white solid. A solution of HCl/CH_3OH (0.74 % V/V) was slowly added to dissolve the white solid and the addition was continued until the pH of the solution reached 1. White solid precipitated upon very slow evaporation of methanol. Yield : 0.64 g (55 %). ^{1}H-NMR ($CDCl_3$) (Figure A.14) 9.35 (4H, broad, $ArCH_2NH_2^+$), 7.66 (4H, d, *J* (HH) 8.6 Hz, ArH_AH_B), 7.08 (4H, d, *J* (HH) 8.6 Hz, ArH_AH_B), 7.96 (2H, s, ArO*H*), 7.02 (4H, s, HOAr*H*), 6.91 (4H, s, ROAr*H*), 4.37 and 3.32 (AB system, 8H, *J* (HH) 12.9 Hz, $ArCH_AH_BAr$), 4.65 and 4.29 (12H, broad, OCH_2CH_2O and $ArCH_2N^+$), 3.92 (4H, broad, NCH_2CH_2S), 2.96 (4H, broad, NCH_2CH_2S, 2.46 (4H, broad, $SCH_2CH_2CH_2S$), 1.89 (2H, broad, $SCH_2CH_2CH_2S$), 1.22 (18H, s, HOAr-*t*-C_4H_9), 1.06 (18H, s, ROAr-*t*-C_4H_9). FAB m/z 1108.2 (M^+). Anal. Calcd. For $C_{69}H_{92}O_6N_2S_2Cl_2$: C, 70.20 ; H, 7.86 ; N, 2.37. Found : C, 70.38 ; H, 7.47 ; N, 2.31.

3.2 Potentiometric Titration

3.2.1 Preparation of the Solutions

There were two different inert background electrolytes that were used in this research. One was tetramethylammoniumchloride (NMe_4Cl, Merck) and the another one was tetrabutylammoniumtrifluoromethanesulfonate ($NBu_4CF_3SO_3$, Fluka). The first electrolyte was prepared by dissolution of a weighted quantity of NMe_4Cl in the mixture of 10% CH_2Cl_2/CH_3OH. The ionic strength was kept constant at $1.0x10^{-2}$ M for the experiments that related to this inert background electrolyte. In the same manner, the latter electrolyte was prepared by dissolution of a weighted quantity of $NBu_4CF_3SO_3$ in the mixture of 10% CH_2Cl_2/CH_3OH. However, the ionic strength was kept constant at $5.0x10^{-2}$ M for all experiments concerned with this inert

background electrolyte. The metal salts used for preparing metal solutions, $Cu(CF_3SO_3)_2$ (Analar grade, Aldrich), $Zn(CF_3SO_3)_2$ (Analar grade, Aldrich), $CdCl_2$ (Merck) and $Hg(CF_3SO_3)_2$ (Strem) were vacuum dried and kept in a dessicator before used. The solution of metal ions Cu^{2+}, Zn^{2+}, Cd^{2+} and Hg^{2+} were prepared by dissolution of weighted quantities of dried metal salts in each inert background solution. The stock solution of Cu^{2+}, Zn^{2+} and Cd^{2+} were $1.0x10^{-2}$ M while that of Hg^{2+} was $5.0x10^{-3}$ M. The solution of **7** and **8** were prepared in each inert background solution. The concentrations of these ligands were $4x10^{-4}$ M in the solution of NMe_4Cl and $1x10^{-3}$ M in the solution of $NBu_4CF_3SO_3$. Tetramethyammonium hydroxide (NMe_4OH, Merck) ($2.5x10^{-2}$ M) and tetrabutylammoniumhydroxide (Bu_4NOH, Aldrich) ($5.0x10^{-2}$ M) in NMe_4Cl and $NBu_4CF_3SO_3$ solution were used as titrant bases. A standard solution of HCl ($1.0x10^{-2}$ M) and $HClO_4$ ($1.0x10^{-2}$) in NMe_4Cl and $NBu_4CF_3SO_3$ solutions were used to adjust the pH of the solution during titration experiments.

3.2.2 Stability Constant Determination

The compounds **7** and **8** were then used for protonation and complexation studies of the neutral derivatives, 25,27-((2,2′-diethoxy)benzyl)-3,7-dithianonane-1,9-diimine-*p*-*tert*-butylcalix[4]arene, **9** and 25,27-((4,4′-diethoxy)benzyl)-3,7-dithianonane-1,9-diimine-*p*-*tert*-butylcalix[4]arene, **10**. The protonation constants of the ligands **9** and **10** in both inert background solutions and the stability constants of the ligands with Cu^{2+}, Zn^{2+}, Cd^{2+} and Hg^{2+} ions in $NBu_4CF_3SO_3$ solutions were determined from potentiometric titration data by a computer program of SUPERQUAD. The electrode was calibrated before use by a standard procedure[28]. For each titration, mole ratio of ligand to proton in NMe_4Cl and $NBu_4CF_3SO_3$

electrolytes were adjusting by HCl and $HClO_4$ solutions, respectively. The experimental data were shown in Table 3.1 for experiments run in the solution of NMe_4Cl and Table 3.2 for experiments run in the solution of $NBu_4CF_3SO_3$. For complexation constant determination, typically 10 ml of the stock solution of a ligand was added with the metal solutions by varying mole ratio of metals : ligands, and pH was adjusted by adding the solution of $HClO_4$. The experimental data for complexation studies with Cu^{2+}, Zn^{2+}, Cd^{2+} and Hg^{2+} were shown in Tables 3.3, 3.4, 3.5 and 3.6, respectively.

Table 3.1 Experimental data used in computer refinements for determining the protonation constants of the compounds **9** and **10** (L) in 10% CH_2Cl_2/CH_3OH (25 °C) using $1.0x10^{-2}$ M NMe_4Cl as electrolyte.

ligand	titration	initial concentration (mM)		pH range	number of data (points)
		L	proton		
7	1	0.367	2.293	2.810 – 12.676	59
	2	0.337	2.102	2.906 – 12.691	63
	3	0.385	1.586	3.232 – 12.998	63
8	1	0.400	1.355	3.296 – 12.396	68
	2	0.400	1.355	3.161 – 12.174	63
	3	0.400	1.355	3.198 – 12.247	67

Table 3.2 Experimental data used in computer refinements for determining the protonation constants of the compounds **9** and **10** (L) in 10% CH_2Cl_2/CH_3OH (25 °C) using $5.0x10^{-2}$ M $NBu_4CF_3SO_3$ as electrolyte.

ligand	titration	initial concentration (mM)		pH range	number of data (points)
		L	proton		
7	1	0.770	3.858	2.606 – 12.135	64
	2	0.909	2.739	3.053 – 12.322	64
	3	0.953	2.384	3.375 – 12.448	64
8	1	0.954	2.390	3.436 – 12.248	59
	2	0.834	3.344	2.744 – 12.215	64
	3	0.770	3.860	2.583 – 12.097	61

Table 3.3 Experimental data used in computer refinements for determining the stability constants of the compounds **9** and **10** (L) with Cu^{2+} in 10% CH_2Cl_2/CH_3OH (25 °C) using $5.0x10^{-2}$ M $NBu_4CF_3SO_3$ as electrolyte.

ligand	titration	initial concentration (mM)			pH range	number of data (points)
		L	proton	Cu^{2+}		
7	1	0.769	3.085	0.775	2.699 – 11.647	67
	2	0.800	3.009	0.403	2.762 – 11.675	69
	3	0.784	3.146	0.593	2.809 – 11.642	68
8	1	0.785	3.147	0.593	2.713 – 11.873	62
	2	0.771	3.086	0.775	2.819 – 12.313	61
	3	0.801	3.210	0.403	2.907 – 12.320	68

Table 3.4 Experimental data used in computer refinements for determining the stability constants of the compounds **9** and **10** (L) with Zn^{2+} in 10% CH_2Cl_2/CH_3OH (25 °C) using $5.0x10^{-2}$ M $NBu_4CF_3SO_3$ as electrolyte.

ligand	titration	initial concentration (mM)			pH range	number of data (points)
		L	proton	Zn^{2+}		
7	1	0.769	3.085	0.776	3.141 – 11.414	54
	2	0.791	3.409	0.594	2.994 – 11.482	52
	3	0.807	3.261	0.403	3.286 – 11.407	48
8	1	0.783	3.242	0.776	2.813 – 11.513	52
	2	0.807	3.265	0.403	2.786 – 11.540	52
	3	0.785	3.396	0.594	3.156 – 11.500	49

Table 3.5 Experimental data used in computer refinements for determining the stability constants of the compounds **9** and **10** (L) with Cd^{2+} in 10% CH_2Cl_2/CH_3OH (25 °C) using $5.0x10^{-2}$ M $NBu_4CF_3SO_3$ as electrolyte.

ligand	titration	initial concentration (mM)			pH range	number of data (points)
		L	proton	Cd^{2+}		
7	1	0.776	3.137	0.785	3.028 – 11.663	54
	2	0.807	3.262	0.408	2.993 – 11.761	54
	3	0.791	3.409	0.601	2.905 – 11.545	51
8	1	0.771	3.126	0.785	2.712 – 10.456	45
	2	0.954	1.908	0.476	4.318 – 11.559	46
	3	0.636	1.664	0.486	3.621 – 11.655	51

Table 3.6 Experimental data used in computer refinements for determining the stability constants of the compounds **9** and **10** (L) with Hg^{2+} in 10% CH_2Cl_2/CH_3OH (25 °C) using $5.0x10^{-2}$ M $NBu_4CF_3SO_3$ as electrolyte.

ligand	titration	initial concentration (mM)			pH range	number of data (points)
		L	proton	Hg^{2+}		
7	1	0.721	2.913	0.731	2.752 – 11.671	62
	2	0.776	3.137	0.394	2.834 – 11.662	58
	3	0.747	3.021	0.569	2.763 – 11.600	55
8	1	0.727	2.926	0.731	2.765 – 11.701	56
	2	0.783	3.137	0.394	2.775 – 11.660	56
	3	0.754	3.034	0.569	3.076 – 11.754	55

The experimental data were evaluated by SUPERQUAD, which refines the logarithm of overall equilibrium constants (log β). For the determination of stability constants of the ligand L with transition metal ions, these stability constants were calculated together with protonation constants of the ligand **L** which were previously obtained from the titration of the ligand **L** in the absence of metal ions. The protonation constants of the ligand **L** were settled as constant during the refinement procedure. The metal hydroxide species, $\mathbf{MOH^+}$, and autoprotolysis constant of methanol (K_{MeOH}) were also included in the computational process in order to precisely obtain stability constants of the complexes.