CHAPTER II

EXPERIMENTAL SECTION

2.1 General procedures

2.1.1 Analytical instrument

Nuclear Magnetic Resonance (NMR) spectra were recorded on a Varian 200, 400 and a Bruker DRX 400 MHz nuclear magnetic resonance spectrometers. In all cases, samples were dissolved in deuterated chloroform, except ligand **5b** (dissolved in DMSO-d_6). The chemical shifts were recorded in part per million (ppm) using a residue proton solvents as internal reference. Elemental analysis were carried out on CHNS/O analyzer (Perkin Elmer PE2400 series II). EI Mass spectrra were recorded on a Bruker Mass spectrometer. Absorption spectra were measured by a Varian Cary 50 UV-vis spectrophotometer. All melting points were obtained on an Electrothermal 9100 apparatus.

2.1.2 Materials

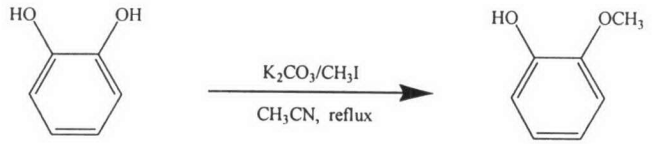
Unless otherwise specified, the solvent and all materials were reagent grades purchased form Fluka, BHD, Aldrich, Carlo Erba, Merck or J.T. Baker and were used without further purification. Commercial grade solvents such as acetone, dichloromethane, hexane, methanol and ethylacetate were purified by distillation before used. Acetonitrile and dichloromethane for set up the reaction were dried over calcium hydride and freshly distilled under nitrogen atmosphere prior to use.

Column chromatography were carried out on silica gel (Kieselgel 60, 0.063-0.200 nm, Merck) Thin layer chromatography (TLC) were performed on silica gel plates (Kieselgel 60, F_{254}, 1mm, Merck). Compound on TLC plates were detected by the UV-light. All manipulations were carried out under nitrogen atmosphere.

All synthesized compounds were characterized by ^{1}H-NMR spectroscopy, mass spectroscopy and elemental analysis.

2.2 Synthesis

2.2.1 Preparation of *o*-methoxy phenol (1a)



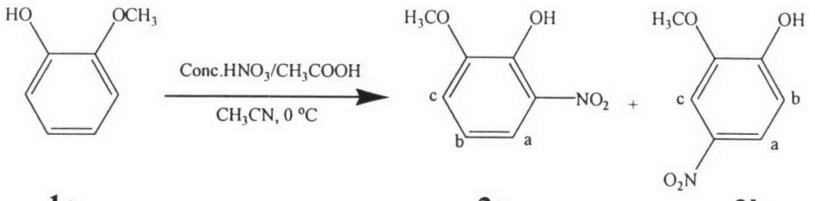
1a

Into a 250 mL two-necked round bottom flask equipped with a magnetic bar and a reflux condenser, pyrocatechol (5.50 g, 0.05 mol), potassium carbonate anhydrous (3.45 g, 0.025 mol) and acetonitrile (100 mL) were mixed and stirred. Iodomethane (4.65 mL, 0.5 mol) in acetonitrile (50 mL) was added slowly dropwise to the mixture. The reaction mixture was refluxed under nitrogen atmosphere for 8 hours and then allowed to cool to room temperature. The solvent was then removed by evaporation. The residue was dissolved in dichloromethane (50 mL) and treated with 3M hydrochloric acid (50 mL) and extracted with dichloromethane (3x50 mL). The organic layer was dried over anhydrous sodium sulfate, filtered and evaporated to dryness to obtain brownish yellow oil. The residue was purified by silica gel column and eluted with dichloromethane. The desired product *o*-methoxy phenol **(1a)** (5.34 g, 85%) was obtained as yellowish oil.

Characterization data for 1a

^{1}H-NMR spectrum (200 MHz, $CDCl_3$) δ (ppm) = 6.85-6.97 (m, 4H, Ar*H*); 5.70 (s, 3H, Ar*OH*); 3.87 (s, 3H, ArOCH_3)

2.2.2 Preparation of 2-metoxy-4-nitrophenol (2b)



1a **2a** **2b**

A mixture of *o*-methoxy phenol **(1a)** (6.1 g, 0.05 mol), acetonitrile (100 mL) and glacial acetic acid (50 mL) was stirred in a 500 mL two-necked round bottom flask at room temperature. A solution of concentrated nitric acid (65%, 3.64 mL, 0.05 mol) in acetonitrile (50 mL) was then added dropwise over 30 minutes and refluxed gently under nitrogen. After 3 hours, the reaction mixture was poured into ice/water (250 mL) and the resulting mixture was adjusted to pH 9 with saturated aqueous sodium hydrogencarbonate and extracted with dichloromethane (3x50 mL). The combined organic phase was dried over anhydrous sodium sulfate. Sodium sulfate was filtered off. The filtrate was concentrated on a rotatory evaporator to obtain brownish orange oil. The residue was placed on a silica gel column. Both 2-methoxy-6-nitrophenol **(2a)** and 2-methoxy-4-nitrophenol **(2b)** were eluted with dichloromethane. The collected fraction of **2a** and **2b** compound were slowly evaporated and hexane was added to afford an orange crystalline solid (0.676 g, 8%) and a yellowish-needle crystalline solid (3.88 g, 46 %), respectively.

Characterization data for 2a

^{1}H-NMR spectrum (200 MHz, $CDCl_3$) δ (ppm) = 10.75 (s, 1H, Ar*OH*); 7.69 (dd, *J* = 7.16, 1.54 Hz, 1H, ArH_a); 7.15, 7.10 (d, each, *J* = 1.42, 1.34 Hz, 1H, ArH_b); 6.92 (d, *J* = 8.62 Hz, 1H, ArH_c); 3.92 (s, 3H, ArOCH_3)

Characterization data for 2b

^{1}H-NMR spectrum (400 MHz, $CDCl_3$) δ (ppm) = 7.93 (dd, *J* = 6.4, 2.4 Hz, 1H, ArH_a); 7.81 (d, *J* = 2.4 Hz, 1H, ArH_b); 7.03 (d, *J* = 8.8 Hz, 1H, ArH_c); 6.22 (s, 1H, Ar*OH*); 4.04 (s, 3H, ArOCH_3)

EI Mass (m/z): 169

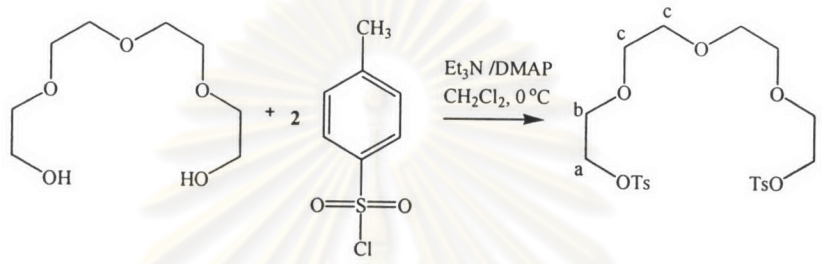
Elemental analysis:

Anal Cald for **2a** ($C_7H_7NO_4$): C, 49.17; H, 4.71; N, 8.28

Found: C, 49.42; H, 4.03; N, 8.00

mp. 99.2-99.6 °C

2.2.3 Preparation of tetraetylene glycol ditosylate

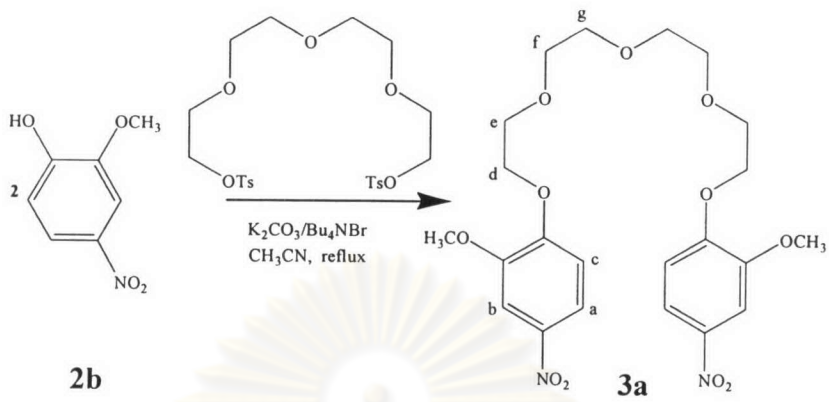


In a 250 mL two-necked round bottom flask, a dichloromethane solutoin (50 mL) of tetraethylene glycol (9.71 g, 0.05 mol), triethylamine (15 g, 0.15 mol) and a catalyst amount of DMAP was chilled to 10 °C with an ice bath and stirred under nitrogen for 30 minutes. A solution of toluene sulfonyl chloride (19.06 g, 0.10 mol) in dichloromethane (100 mL) was then added dropwise. The reaction mixture was allowed to stir overnight at room temperature under nitrogen. After the reaction was completed, the mixture was then poured into an aqueous solution of 3 M hydrochloric acid (100 mL) and stirred for 30 minutes and then extracted with dichloromethane (3x50 mL). The organic layer was dried over anhydrous sodium sulfate, filtered and evaporated to dryness. The residue was purified by column chromotography and eluted with dichloromethane. The desired product tetraethylene glycol ditosylate (21.59 g, 86%) was obtained as colorless oil.

Characterization data for tetraethylene glycol ditosylate

^{1}H-NMR spectrum (200 MHz, $CDCl_3$) δ (ppm) = 7.73 and 7.30 (d, each, J = 14.76 Hz, 8H, Ar*H*); 4.09 (m, 4H, ArCH_{2a}); 3.60 (m, 4H, ArOCH_2CH_{2b}); 3.54 (s, 8H, Ar$O(CH_2)OCH_{2c}$); 2.39 (s, 3H, ArCH_3)

2.2.4 Preparation of 2,2′-[oxabis(4-oxapentaethyleneoxy)]-bis(2-methoxy-4-nitrophenol) (3a)



A suspension of 2-methoxy-4-nitrophenol **(2b)** (0.24 g, 0.0014 mol), catalyst amount of tetrabutylammonium bromide and potassium carbonate anhydrous (0.98 g, 0.007 mol) in acetonitrile (50 mL) was stirred in a 250 mL two-necked round bottom flask. Then a solution of tetraethylene glycol ditosylate (0.35 g, 0.0007 mol), in acetonitrile (50 mL) was added dropwise and refluxed under nitrogen atmosphere for 5 days. The mixture turned yellow and was allowed to cool to room temperature. The solvent was then removed under reduced pressure. The residue was dissolved in 50 mL of dichloromethane and the solution was treated with 3 M hydrochloric acid (50 mL) and extracted with dichloromethane (3x50 mL). The combined organic phase was dried over sodium sulfate anhydrous. The solvent was evaporated to dryness; the residue was dissolved in a minimum amount of dichloromethane and added with methanol. The solution was allowed to stand overnight at room temperature to allow a slow evaporation of the solvent. The desired product 2,2′-[oxabis(4-oxapentamethleneoxy)]-bis(2-methoxy-4-nitrophenol) **(3a)** was slowly crystallized from the solution as a bright yellow crystalline solid (0.60 g, 85%).

Characterization data for 3a

^{1}H-NMR spectrum (400 MHz, $CDCl_3$) δ (ppm) = 7.91 (dd, J = 6.4, 2.4 Hz, 2H, ArH_a); 7.76 (d, J = 2.8 Hz, 2H, ArH_b); 6.98 (d, J = 8.8 Hz, 2H, ArH_c); 4.31 (t, J = 4.4 Hz, 4H, ArOCH_{2d}); 3.96 (s, 3H, ArOCH_3); 3.77 (broad, 4H, ArOCH2CH_{2e}); 3.76 (m, 4H, ArOCH$_2$CH$_2$OCH_{2f}); 3.71 (m, 4H, ArOCH$_2$CH$_2$OCH$_2$$CH_{2g}$)

EI MS (m/z): 496

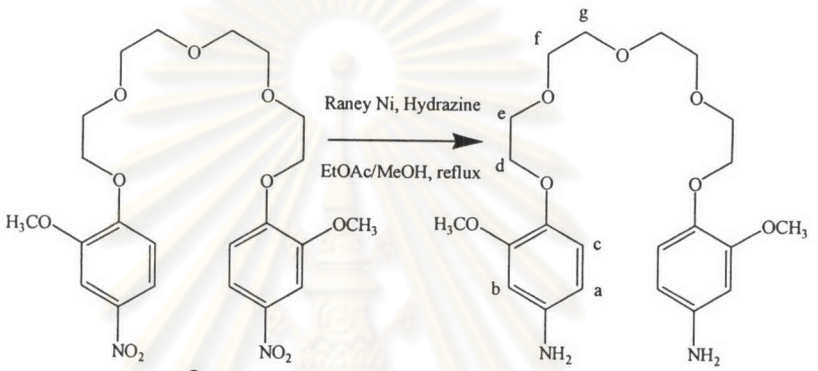
Elemental analysis:

Anal Cald for **3a** ($C_{22}H_{28}N_2O_{11}$): C, 53.22; H, 5.68; N, 5.64

Found: C, 53.22; H, 5.63; N, 5.74

mp. 102-103 °C

2.2.5 Preparation of 2,2′-[oxabis(3-oxapentaethyleneoxy)]-bis(2-methoxy-4-aminophenol) (4a)



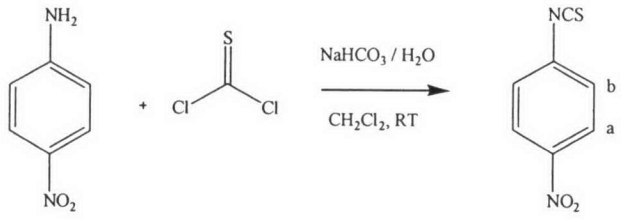
3a **4a**

A mixture of **3a** (0.30g, 0.006 mol) and of Raney nickel (0.44 g as catalyst) was stirred in a 25 mL two necked round bottom flask under nitrogen. Hydrazine hydrate (1.7 mL, 0.03 mol) was added slowly and the mixture was refluxed. Evolution of hydrogen was observed during the addition of hydrazine. When the addition completed, stirring was continued for 2 hours. The solution was allowed to cool to room temperature. The catalyst was then removed by filtration and washed with dichloromethane. The combined filtrate was concentrated under reduced pressure and extracted with dichloromethane (3x25 mL). The combined organic layer was dried over anhydrous sodium sulfate, filtered and evaporated to dryness to obtain the desired product **(4a)** as yellow oil.

Characterization data for 4a

^{1}H-NMR spectrum (400 MHz, $CDCl_3$) δ (ppm) = 6.76 (dd, *J* = 6.4, 2.4 Hz, 2H, ArH_a); 6.25(s, 2H, ArH_b); 6.14 (dd, *J* = 6.2, 2.4 Hz, 2H, ArH_c); 4.04 (m, 4H, ArOCH_{2d}); 3.90 (s, broad, 4H, ArNH_2); 3.80 (m, 4H, ArOCH2CH_{2e}); 3.74 (s, 3H, ArOCH_3); 3.69 (m, 4H, $ArOCH_2CH_2OCH_{2f}$); 3.63 (m, 4H, $ArOCH_2CH_2OCH_2CH_{2g}$)

2.2.6 Preparation of *p*-nitrophenyl thioisocyanate[45]



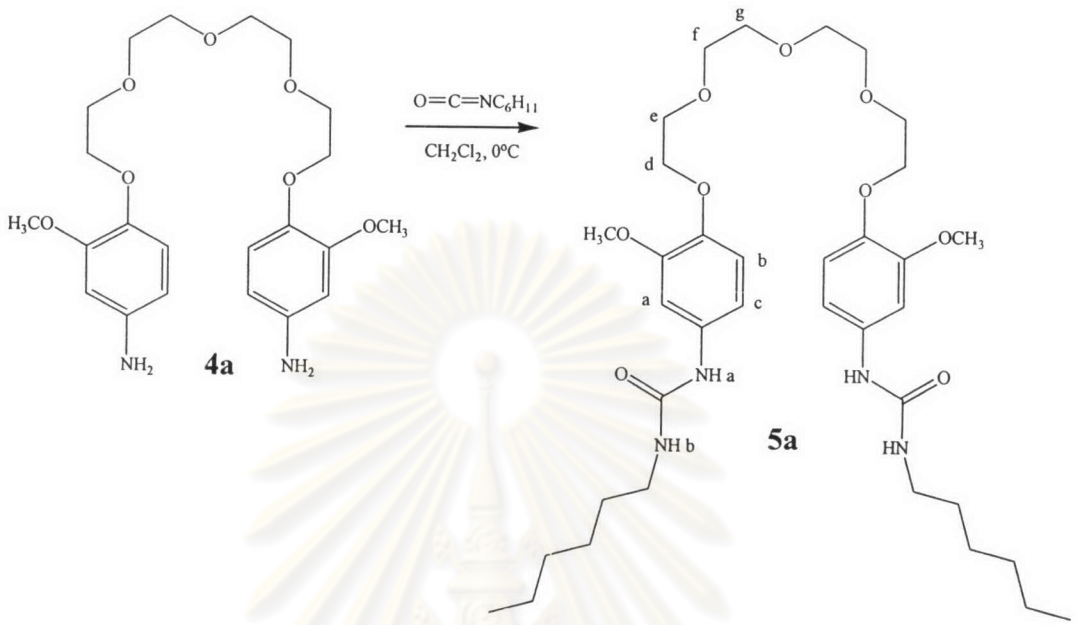
A mixture of 4-nitroaniline (0.7163 g, 0.005 mol) and sodium hydrogen carbonate (0.9872 g, 0.011 mol) in dichloromethane: water (20:10 mL) was stirred in a 50 mL round bottom flask at room temperature. A solution of thiophosgene (0.6 mL, 0.0078 mol) in dichloromethane (5 mL) was then added. The mixture was allowed to stand overnight under nitrogen atmosphere. After the reaction was completed, the mixture was then extracted with dichloromethane (3x25 mL). The organic layer was dried over anhydrous sodium sulfate, filtered and evaporated to dryness. The residue was dissolved in a minimum amount of dichloromethane and methanol/hexane was added to precipitate a yellow crystalline solid (0.86 g, 93%).

Characterization data for *p*-nitrophenyl thioisocyanate

^{1}H-NMR spectrum (200 MHz, $CDCl_3$) δ (ppm) = 8.22 (d, J = 6.97 Hz, 2H, ArH_a); 7.33 (d, J = 5.12 Hz, 2H, ArH_b)

mp. 113-114 °C

2.2.7 Preparation of acyclic crown ether containing hexyl urea moieties (5a)



Under nitrogen, a solution of **4a** (0.12 g, 0.0003 mol) in dichloromethane 10 mL was placed in a 50 mL two necked round bottom flask and cooled to 0 °C. A solution of hexyl isocyanate (0.08 mL, 0.006 mol) was then added slowly while keeping the solution temperature at 0 °C. The solution was stirred for 3 hours at 0 °C and then for another 12 hours at room temperature. The precipitate formed was then filtered off and dissolved in a minimum amount of dichloromethane. Hexane was added to precipitate the desired product as a white powder (0.13 g, 68 %).

Characterization data for 5a

^{1}H-NMR spectrum (400 MHz, $CDCl_3$) δ (ppm) = 6.97 (d, *J* = 2.0 Hz, 2H, ArH_a); 6.68 (d, *J* = 8.4 Hz, 2H, ArH_b); 6.58 (s, each, 2H, NH_a); 6.44 (d, *J* = 8.8 Hz, 2H, ArH_c); 5.01 (t, broad, 2H, NH_b); 4.02 (m, 4H, ArOCH_{2d}); 3.76 (m, 4H, ArOCH$_2$CH_{2e}); 3.70 (s, 6H, ArOCH_3); 3.62 (m, 4H, ArOCH$_2$OCH_{2f}); 3.59 (m, 4H, ArO(CH$_2$)$_2$OCH$_2$CH_{2g}); 3.16 (m, 4H, -NH$_b$CH_2(CH$_2$)$_4$CH$_3$); 1.42 (m, 4H, -NH$_b$CH$_2$CH_2(CH$_2$)$_2$CH$_3$); 1.22 (m, 4H, -NH$_b$(CH$_2$)$_2$(CH_2)$_3$CH$_3$); 0.80 (m, 6H, -NH$_b$(CH$_2$)$_5$CH_3)

ES$^+$ Mass (m/z)**:** 691.4

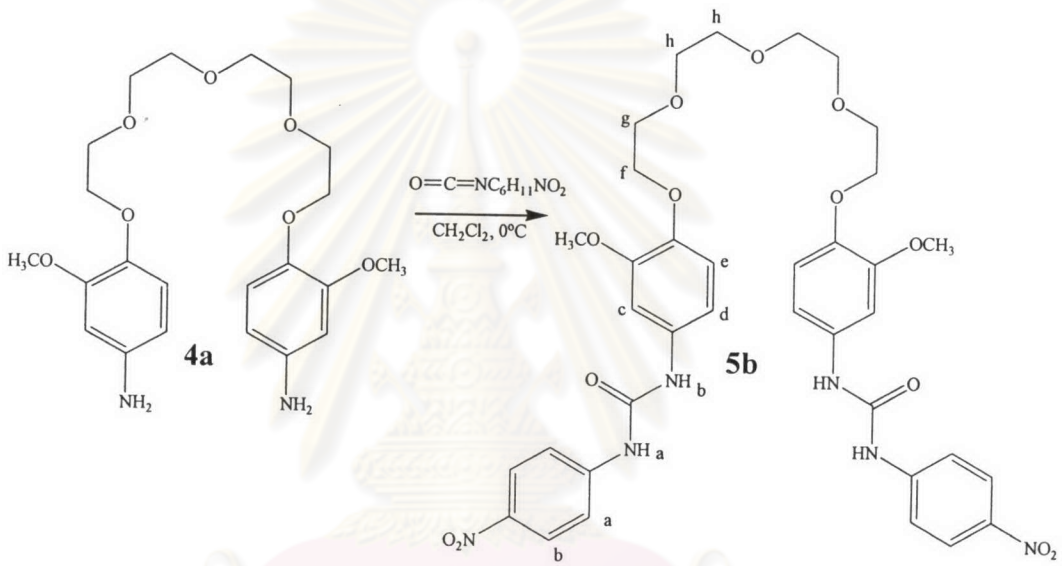
Elemental analysis:

Anal Cald for **5a** ($C_{36}H_{58}N_4O_9$): C, 62.59; H, 8.46; N, 8.11

Found: C, 62.63; H, 8.49; N, 8.16

mp. 144-145 °C

2.2.8 Preparation of acyclic crown ether contaning nitrophenyl thiourea moieties (5b)



Under nitrogen, a solution **4a** (0.26 g, 0.0006 mol) in dichloromethane (10 mL was placed in a 50 mL) two necked round bottom flask and cooled to 0 °C. A solution of *p*-nitrophenyl thioisocyanate (0.24 g, 0.0013 mol) was then added slowly while keeping the solution temperature at 0 °C. The reaction solution was stirred for 3 hours at 0 °C and then for another 12 hours at room temperature. The precipitate was then filtered off and dissolved in a minimum amount of dimethylsulfoxide. Methanol was added to precipitate the desired product as a bright yellow solid (0.22 g, 46%)

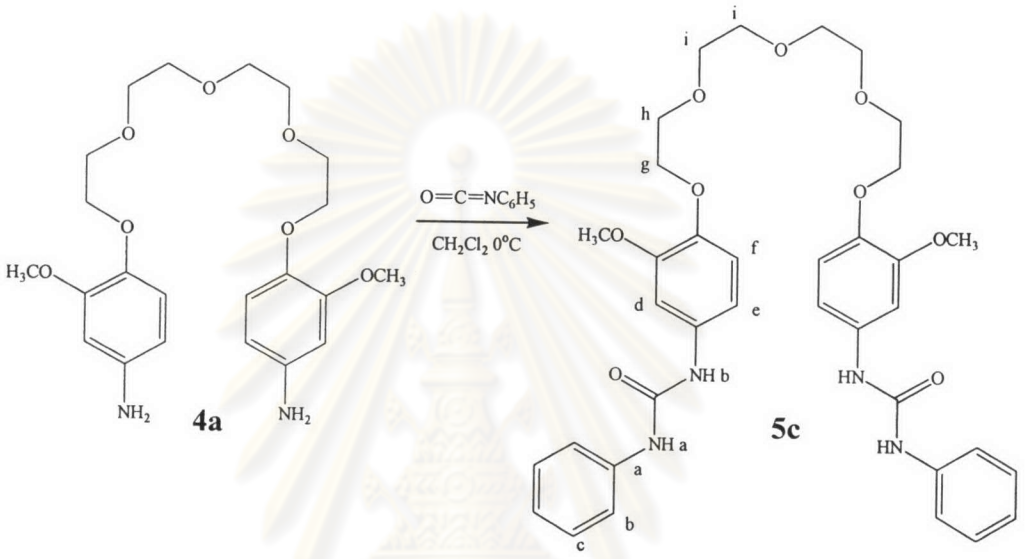
Characterization data for 5b

^{1}H-NMR spectrum (300 MHz, $CDCl_3$) δ (ppm) = 10.19 (s, 2H, NH_a); 10.10 (s, 2H, NH_b); 8.19 (d, J = 7.67 Hz, 4H, ArH_a); 7.80 (d, J = 7.64 Hz, 4H, ArH_b); 7.11 (s, 2H, ArH_c); 6.92 (s, br, 4H, ArH_d, ArH_e); 4.05 (t, broad, 4H, ArOCH_{2f}); 3.71 (s, 6H, ArOCH_3); 3.56 (m, 4H, ArOCH$_2CH_{2g}$); 3.44-3.30 (m, 8H, ArO(CH$_2$)$_2$OCH_{2h})

ES$^+$ Mass (m/z)**:** 797.2

mp. 142-144 °C

2.2.9 Preparation of acyclic crown ether containing phenyl urea moieties (5c)



Under nitrogen, a solution of **4a** (0.186 g, 0.0004 mol) in dichloromethne (10 mL was placed in a 50 mL) two necked round bottom flask and cooled to 0 °C. A solution of phenyl isocyanate (0.10 mL, 0.0009 mol) was then added slowly while keeping the solution temperature at 0 °C. The reaction was stirred for 3 hours at 0 °C and then for another 12 hours at room temperature. The precipitate was filtered off and dissolved in a minimum amount of dichloromethane. Hexane was added to precipitate the desired product as a white powder (0.26 g, 90%).

Characterization data for 5c

^{1}H-NMR spectrum (400 MHz, $CDCl_3$) δ (ppm) = 7.58 (s, 2H, NH_a); 7.39-7.38 (m, 6H, ArH_a, ArH_c); 7.29 (merge with solvent peak, 2H, ArH_d); 7.28 (s, 2H, NH_b); 7.08 (m, br, 4H, ArH_b); 6.75 (d, J = 9.2 Hz, 2H, ArH_e); 6.56 (d, J = 9.2 Hz, 2H, ArH_f); 4.06 (t, J = 6.0 Hz, 4H, ArOCH_{2g}); 3.84 (t, J = 5.8 Hz, 4H, ArOCH$_2CH_{2h}$); 3.74 (s, 6H, ArOCH_3); 3.72 (s, 4H, ArOCH$_2$CH$_2$OCH_{2i})

mp. 168-169 °C

2.3 Complexation studies of ligand 5a by ^{1}H-NMR titrations

2.3.1 Cation complexation studies of ligand 5a with Na^+ and K^+

Typically, a solution of 0.005 M of ligand **5a** (0.001727 g, 2.5 X 10^{-6} mol) in $CDCl_3$ (0.5 mL) was prepared in a NMR tube. A solution of 0.05 M of a metal cation as perchlorate salt in CD_3CN (0.25 mL) was prepared in a vial and added directly to the NMR tube by a microsyringe to have guest:host ratios shown in Table 2.1. ^{1}H-NMR spectra were recorded after each addition with chemical shifts referred to a residue proton signal.

Table 2.1 Amounts of solutions of cations used to prepare various cation: ligand **5a** ratios

ratio of cation:ligand **5a**	volume cation added (μL)	[ligand **5a**]	[cation]
0.0:1.0	0	0.00050	0
0.1:1.0	5	0.00495	0.00049
0.2:1.0	5	0.00490	0.00098
0.3:1.0	5	0.00485	0.00146
0.4:1.0	5	0.00481	0.00192
0.5:1.0	5	0.00476	0.00238
0.6:1.0	5	0.00472	0.00283
0.7:1.0	5	0.00467	0.00327
0.8:1.0	5	0.00463	0.00370
0.9:1.0	5	0.00459	0.00413
1.0:1.0	5	0.00454	0.00454
1.2:1.0	10	0.00446	0.00536
1.4:1.0	10	0.00439	0.00614
1.6:1.0	10	0.00431	0.00689
1.8:1.0	10	0.00424	0.00763
2.0:1.0	10	0.00417	0.00833
3.0:1.0	50	0.00385	0.01154
4.0:1.0	50	0.00357	0.01429

2.3.2 Anion complexation studies of ligand 5a with various anions such as chloride, bromide, iodide, nitrate, benzoate, acetate and dihydrogen phosphate

Typically, a solution of 0.005 M of ligand **5a** (0.001727g, 2.5 X 10^{-6} mol) in $CDCl_3$ (0.5 mL) was prepared in a NMR tube. A solution of 0.05 M of an anion as tetrabutylammonium salt in $CDCl_3$ (0.25 mL) was prepared in a vial and added directly to the NMR tube by a microsyringe to have guest:host ratios shown in Table 2.2. ^{1}H-NMR spectra were recorded after each addition with chemical shifts referred to a residue proton signal.

2.3.3 Complexation studies of ligand 5a in the presence of 2 equivalents of $NaClO_4$ with various anions such as chloride, bromide, iodide, nitrate, benzoate, acetate and dihydrogen phosphate

Typically, titration experiments were carried out by addition an acetonitrile-d_3 solution (0.05 mL) of 0.1 M $NaClO_4$ to a solution of ligand **5a** (0.001727 g, 2.5 X 10^{-6} mol) in $CDCl_3$ (0.45 mL) into NMR tube. A solution of 0.05 M of an anion as tetrabutylammonium salt in $CDCl_3$ (0.25 mL) was prepared in a vial and added directly to the NMR tube by a microsyringe to have guest:host ratios shown in Table 2.2. ^{1}H-NMR spectra were recorded after each addition with chemical shifts referred to a residue proton signal.

2.3.4 Complexation studies of ligand 5a in the presence of 1.2 equivalents of an anion such as chloride, bromide, iodide, nitrate, benzoate, acetate and dihydrogen phosphate with Na^+

Typically, the titration experiments were carried out by addition of an $CDCl_3$ solution (0.1 mL) of 0.03 M anion as tetrabutylammonium salt to a solution of ligand **5a** (0.001727 g, 2.5 X 10^{-6} mol) in $CDCl_3$ (0.40 mL) to a NMR tube. A solution of 0.05 M $NaClO_4$ in CD_3CN (0.25 mL) were prepared in a vial and added directly to the NMR tube by a microsyringe to have guest:host ratios shown in Table 2.2. ^{1}H-NMR spectra were recorded after each addition with chemical shifts referred to a residue proton signal.

Table 2.2 Amounts of solutions of guests used to prepare various cation: ligand **5a** ratios for complexation studies in cases of **2.3.2**, **2.3.3** and **2.3.4**[*]

ratio of guest:ligand 5a	volume guest added (μl)	[ligand 5a]	[guest]
0.0:1.0	0	0.00050	0
0.1:1.0	5	0.00495	0.00049
0.2:1.0	5	0.00490	0.00098
0.3:1.0	5	0.00485	0.00146
0.4:1.0	5	0.00481	0.00192
0.5:1.0	5	0.00476	0.00238
0.6:1.0	5	0.00472	0.00283
0.7:1.0	5	0.00467	0.00327
0.8:1.0	5	0.00463	0.00370
0.9:1.0	5	0.00459	0.00413
1.0:1.0	5	0.00454	0.00454
1.3:1.0	10	0.00442	0.00575
1.6:1.0	10	0.00431	0.00689
2.0:1.0	10	0.00417	0.00833
3.0:1.0	50	0.00385	0.01154
4.0:1.0	50	0.00357	0.01429

* The proton signals become too broad to interpret upon addition of more than 2.0:1.0 of the guest:ligand **5a** ratios.

2.4 Complexation studies of ligand 5b by UV-vis titrations

2.4.1 Cation complexation studies of ligand 5b with alkali metal ions such as sodium, potassium, rubidium and cesium.

Typically, a stock solution of $2x10^{-5}$ M of ligand **5b** in DMSO (AR grade) was prepared by adding 1 mL of a stock solution ($2x10^{-4}$ M) of ligand **5b** in a 10 mL volumetric flask. The stock solution of ligand **5b** (2 mL) was added to a 1 cm quartz cuvette. Absorption spectra of ligand **5b** were recorded from 270 nm to 600 nm at ambient temperature with a Varian Cary 50 UV-vis spectrophotometer. A solution of 0.05 M of an alkali metal ion (Na^+ and K^+ as perchlorate salt and Rb^+ and Cs^+ as hexafluorophosphate salt) in DMSO was prepared in a 5 mL volumetric flask. The solution of a guest was added directly to the cuvette by a microburete and stirred for 30 seconds. Absorption spectra were measured after each addition to have guest:host ratios from 0:1 to 1800:1.

2.4.2 Anion complexation studies of ligand 5b with various anions such as chloride, bromide, iodide, nitrate, benzoate, acetate, perchlorate, hexafluorophosphate and dihydrogen phosphate

Typically, a stock solution of $2x10^{-5}$ M of ligand **5b** in DMSO was prepared by adding 2 mL of a stock solution ($2x10^{-4}$ M) of ligand **5b** to a 10 mL volumetric flask. The stock solution of ligand **5b** was added to a 1 cm quartz cuvette. Absorbtion spectra of ligand **5b** were recorded from 270 nm to 600 nm at ambient temperature. A solution of an anion as tetrabutylammonium salt in DMSO was prepared in a 5 mL volumetric flask, which had a concentration as shown in Table 2.3. The solution of a guest was added directly to the cuvette by a microburete and stirred for 30 seconds. Absorption spectra were measured after each addition.

Table 2.3 The concentration of anions that used in anion complexation studies with ligand **5b** and the final ratios of guest:host

anion	[anion] M	final guest:host ratios
Chloride	0.05	1800:1
Bromide	0.05	1800:1
Iodide	0.05	1800:1
Nitrate	0.05	1800:1
Perchlorate	0.05	1800:1
Hexafluorophosphate	0.05	1800:1
Dihydrogen phosphate	0.001	24:1
Benzoate	0.0003	6:1
Acetate	0.001	38:1

2.4.3 Complexation studies of ligand 5b in the presence of 500 equivalents of an alkali metal ion ($NaClO_4$ and $KClO_4$) with various anions such as chloride, bromide, iodide, nitrate, benzoate and dihydrogen phosphate

Typically, a stock solution of 0.01 M of alkali metal ion in a DMSO solution of ligand **5b** ($2x10^{-5}$ M) was prepared by adding 2 mL of a stock solution (0.05 M) of an alkali metal ion and 1 mL of a stock solution of ligand **5b** (2×10^{-4} M) to a 10 mL volumetric flask. The stock solution of ligand **5b** plus an alkali metal ion (2 mL) was added to a 1 cm quartz cuvette. Absorption spectra of ligand **5b** plus a metal ion were recorded from 270 nm to 600 nm at ambient temperature. A solution of an anion as tetrabutylammonium salt in DMSO was prepared in a 5 mL volumetric flask, which had a concentration as shown in Table 2.4. The solution of a guest was added directly to the cuvette by a microburete and stirred for 30 seconds. Absorption spectra were measured after each addition.

Table 2.4 The concentration of anions that used in anion complexation studies with ligand **5b** in the presence of 500 equivalents of an alkali metal ion and the final ratios of guest:host

anion	[anion] M	final guest:host ratios
Chloride	0.05	1800:1
Bromide	0.05	1800:1
Iodide	0.05	1800:1
Nitrate	0.05	1800:1
Dihydrogen phosphate	0.001	28:1
Benzoate	0.0003	9:1

2.4.4 Complexation studies of ligand 5b in the presence of an anion such as chloride, bromide, iodide, nitrate, benzoate and dihydrogen phosphate with Na^+ and K^+

Typically, a stock solution of an anion as tetrabutylammonium salt in a DMSO solution of ligand **5b** ($2x10^{-5}$ M) was prepared by adding 1 mL of a stock solution ($2x10^{-4}$ M) of ligand **5b** and a stock solution of an anion (as shown in Table 2.5) into a 10 mL volumetric flask. Subsequently, the solution had the equivalent of anion per ligand **5b** ratios as shown in Table 2.5. The stock solution of ligand **5b** plus an anion (2mL) was added to a 1 cm quartz cuvette. Absorption spectra of ligand **5b** plus an anion were recorded from 270 nm to 600 nm at ambient temperature. A solution of an alkali metal ion as perchlorate salt in DMSO was prepared in a 5 mL volumetric flask, which had a concentration as shown in Table 2.5. The solution of a guest was added directly to the cuvette by microburete and stirred for 30 seconds. Absorption spectra were measured after each addition.

Table 2.5 The concentration of anions that used in alkali metal ion complexation studies with ligand **5b** in the presence of an anion and the final ratios of guest:host

anion	[anion] M^{-1}	volume anion pipeted (mL)	equivalent anion:ligand	[guest] (M)		guest:host	
				Na^+	K^+	Na^+	K^+
Cl^-	0.1	4.00	2000	0.05	0.05	1800:1	1800:1
Br^-	0.1	4.00	2000	0.05	0.05	1800:1	1800:1
I^-	0.1	4.00	2000	0.05	0.05	1800:1	1800:1
NO_3^-	0.1	4.00	2000	0.05	0.05	1800:1	1800:1
BzO^-	0.01	5.00	10	0.05	0.05	1800:1	1800:1
$H_2PO_4^-$	0.05	5.00	50	0.0015	0.006	240:1	60:1

2.5 Electrochemical studies

2.5.1 Apparatus

Cyclic voltammetry and square wave voltammetry were performed using an AUTOLAB PGSTAT 100 (Ecochemie, Netherland) thermostat with a three electrode consisting of a glassy carbon with a conducting area of 3 mm diameter, a platinum wire counter electrode and a $Ag/AgNO_3$ reference electrode. All scans were carried out at room temperature and scan rates were varied.

2.5.2 Cleaning procedure for electrode

Cleaning of the glassy carbon electrode was done using a BAS polishing kit with stepwise finer abrasives down to 0.03 and 0.1 μM alumina powder slurry. The electrode was then sonicated in 0.005 M H_2SO_4 for 5 minutes and then soaked with dimethylformamide. This cleaning procedure was repeated after each measurement. The platinum wire counter electrode was cleaned by immerged in 3 M HNO_3 for 30 minutes, rinsed with distilled water and wiped to dryness before use. The reference electrode was cleaned by immerging in 3 M HNO_3 for 30 minutes and rinsing with distilled water.

2.5.3 Preparation of the main solution

Unless otherwise indicated, all experiments were carried out in an electrolyte solution of 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) in dimethylformamide. The reference electrode contained 0.01 M $AgNO_3$ in 0.1 M $TBAPF_6$ in dimethylformamide. The background solution contained only 0.1 M $TBAPF_6$ (1.9372 g) in dimethylformamide.

2.5.4 CV and SWV measurements

All CV and SWV measurements were carried out in a cell compartment enclosed with a build-in Teflon cap to avoid the interference from gas oxygen. All solutions were bubbled with nitrogen at least 5 minutes before each measurement.

Cyclic voltammetry were recorded over ranges of scan rates from 0.02 to 1.0 V/s. The values of E_p and I_p were determined graphically from the CV by plotting a tangent to the leading baseline of the peak to correct for the background current. At a scan rate of 0.020 V/s the half-wave potential $E_{1/2}$ was determined as $(E_{pa}+E_{pc})/2$. Square wave voltammograms were recorded at 60 Hz and amplitude 0.030 V.

2.5.5 Cation complexation studies of ligand 5b with Na^+

A solution of 0.001 M of ligand **5b** (0.00398 g, 0.005 mmol) and a solution of $NaClO_4$ (0.06 g, 0.5 mmol) in $TBAPF_6$ in dimethylformamide was prepared in a 5 mL volumetric flask. All solutions were sonicated for 30 minutes befored used. The solution of $NaClO_4$ was added directly to the cell by a microsyringe until no change in redox potential shifts was observed. Redox currents were determined from CV scans of the complex solutions at a scan rate of 0.020 V/s using the method described above.

2.5.6 Anion complexation studies of ligand 5b with various anions such as chloride, bromide, iodide, nitrate, benzoate, acetate and dihydrogen phosphate

Typically, a solution of 0.001 M of ligand **5b** (0.00398 g, 0.005 mmol) and a solution of 0.5 mmol anion as tetrabutylammonium salt in $TBAPF_6$ in dimethylformamide was prepared in a 5 mL volumetric flask. All solutions were sonicated for 30 minutes befored used. The solution of anion was added directly to the cell by a microsyringe until no change in redox potential shifts was observed. Redox

currents were determined from CV scans of the complex solutions at a scan rate of 0.020 V/s using the method described above.

2.5.7 Complexation studies of ligand 5b in the presence of 2 equivalents of $NaClO_4$ with various anions such as benzoate, acetate and dihydrogen phosphate

Typically, a solution of 0.002 M $NaClO_4$ in a solution of 0.001 M ligand **5b** (0.00398 g, 0.005 mmol) in $TBAPF_6$ in dimethylformamide was prepared in a 5 mL volumetric flask. A solution of 0.1 M anion was prepared in $TBAPF_6$ in dimethylformamide in a 5 mL volumetric flask. All solutions were sonicated for 30 minutes before used. The solution of an anion was added directly to the cell by a microsyringe until no change in redox potential shifts was observed. Redox currents were determined from CV scans of the complex solutions at a scan rate of 0.020 V/s using the method described above.

2.5.8 Complexation studies of ligand 5b in the presence of 2 equivalents of an anion such as benzoate, acetate and dihydrogenphosphate with Na^+

Typically, a solution of 0.002 M of an anion in a solution of 0.001 M ligand **5b** (0.00398 g, 0.005 mmol) in $TBAPF_6$ in dimethylsulfoxide was prepared in a 5 mL volumetric flask. A solution of 0.1 M $NaClO_4$ was prepared in supporting electrolyte of $TBAPF_6$ in dimethyformamide in a 5 mL volumetric flask. All solutions were sonicated for 30 minutes befored used. The solution of $NaClO_4$ was added directly to the cell by a microsyringe until no change in redox potential shifts was observed. Redox currents were determined from CV scans of the complex solutions at a scan rate of 0.020 V/s using the method described above.