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Chromogenic macrocyclic derivatives of azoles—synthesis and properties

Ewa Wagner-Wysiecka, Elżbieta Luboch, Marzena Kowalczyk and Jan F. Biernat*

Department of Chemical Technology, Technical University of Gdańsk, ul. Narutowicza 11/12, 80-952 Gdańsk, Poland

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Abstract—The synthesis of macrocyclic chromogenic derivatives of pyrrole and imidazole is described. The complexing properties of these compounds with metal cations were investigated spectrophotometrically in acetonitrile. The synthesized crown ethers were also tested as ion carriers in ion-selective membrane electrodes. The X-ray structure of one isomer of 18-membered pyrrole crown ether is reported.

1. Introduction

Chromoionophores are reagents changing color upon interaction with ions.[1–4] They often consist of a crown ether residue and a chromophore unit, usually located in a side arm. Chromogenic crown ethers in which the chromoionophore composes a part of macrocycle have also been synthesized. To this category belong previously synthesized 18- and 21-membered proton dissociable chromogenic crown ethers: macrocyclic derivatives of *p*-alkylphenols,[5,6] resorcinol[7] and 1,3-dihydroxynaphthalene.[8] Their structures comprise: oxyethylene residues and two azo chromophores forming a macrocycle, and one phenolic –OH group directed inside the cavity. The location of the azo groups enables their direct participation in cation complexation. The phenolic –OH group forms an intramolecular hydrogen bond with one nitrogen atom of the –N=N– group inside the cavity.[6] These reagents show significant spectral differences between the chromogenic compound and its complex. The expected participation of the –N=N– chromophore in cation capture inside the crown ether cavity probably stabilizes the complex formed helping to discriminate between cations according their size. The 18- and 21-membered chromogenic derivatives of *p*-alkylphenol can be used for determination of small amounts of lithium cation.[5,6,9] Analogous 18-membered macrocyclic derivatives of resorcinol and 1,3-dihydroxynaphthalene are lithium selective while 21-membered resorcinol crown ether is sodium selective.[8]

This work describes the synthesis and study of new chromogenic crown reagents in which the phenol residue is replaced by residues of azoles. To the best of our knowledge chromogenic crown ethers with inherent azole residues are not known to date. Considering the similarity of acid–base properties of phenols with structurally related pyrrole and imidazole, we expected for macrocyclic derivatives of the above heterocycles comparable properties as found for *p*-alkylphenol and resorcinol chromoionophores.[10,11]

2. Results and discussion

Azole derivatives were obtained by coupling pyrrole or imidazole with the respective bis-diazonium salts (Scheme 1) by analogy to previously described procedures.[5–8] The coupling reaction performed under high dilution conditions at pH~11 (NaOH) affords higher yield as compared to the yield of chromogenic macrocyclic derivatives of *p*-alkylphenols.

From the reaction mixture 2,3- and 2,5-positional isomers of pyrrole derivatives were isolated and identified among four theoretically possible isomers. The identified isomers could be easily recognized by TLC, e.g. in methylene chloride–methanol (15:2) system. Isomers denoted as **1a** and **2a** are deep red with R_f about 0.8 while compounds denoted as **1b** and **2b** are orange with R_f about 0.3.

For imidazole derivatives one macrocyclic product was identified in each reaction although two isomers are theoretically possible.

In the case of pyrrole and imidazole derivatives the total yield of macrocyclic products generally exceeds 40%. No

Keywords: chromoionophores; azole azocrown ethers; synthesis; complexes; spectrophotometric reagents; ion-selective membrane electrodes; X-ray structure.

* Corresponding author. Tel.: +48-58-3471-949; fax: +48-58-3471-949; e-mail: biernat@chem.pg.gda.pl

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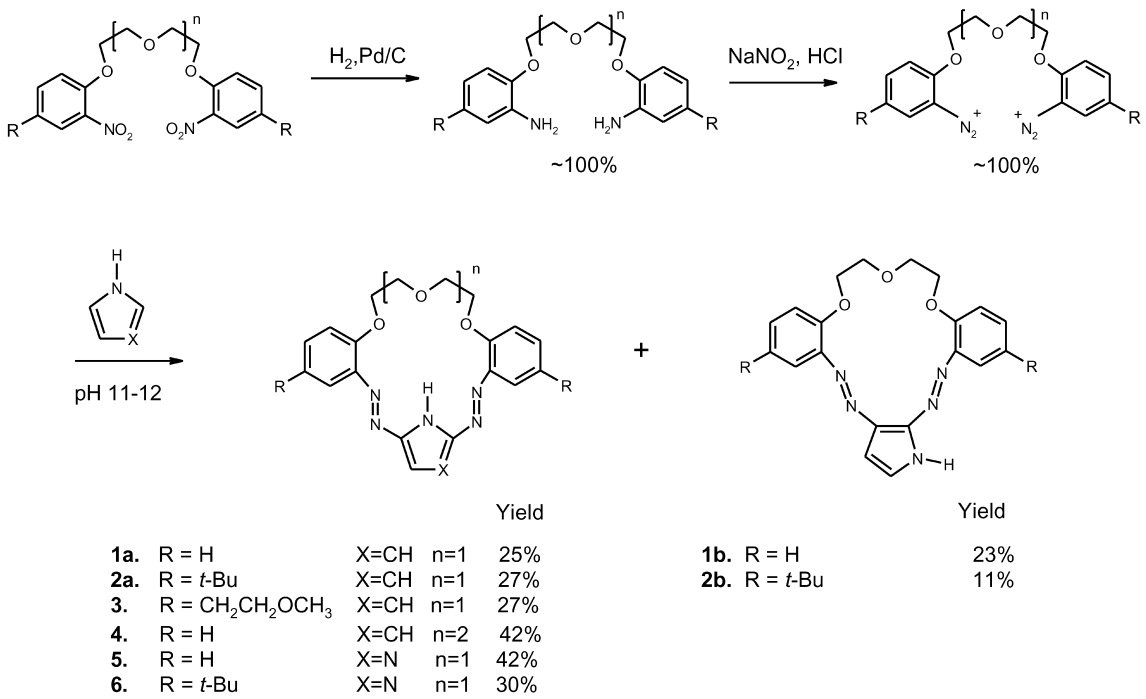

				Yield
1a.	R = H	X=CH	n=1	25%
2a.	R = *t*-Bu	X=CH	n=1	27%
3.	R = $CH_2CH_2OCH_3$	X=CH	n=1	27%
4.	R = H	X=CH	n=2	42%
5.	R = H	X=N	n=1	42%
6.	R = *t*-Bu	X=N	n=1	30%

		Yield
1b.	R = H	23%
2b.	R = *t*-Bu	11%

Scheme 1. Synthesis of macrocyclic azocrown ethers with azole unit.

macrocyclic products were isolated by coupling triazole with bis-diazonium salts.

In the described syntheses, the use of sodium or potassium salts at the coupling stage has no significant influence on the yield.

Properties of the synthesized azocrown ethers **1**–**6** were studied by UV–Vis spectrophotometry. Acid–base properties of azole derivatives were studied either in acetonitrile or in dioxane: water (1:1 v/v) solvent system. Experiments in dioxane–water were performed to compare properties of the new chromogenic azole derivatives with chromogenic alkylphenol azomacrocycles.[5,6] Both under acidic ($HClO_4$) and basic (Me_4NOH) conditions spectral changes were observed only at extreme values of pH. Thus, there was no possibility to determine parameters of the acid–base equilibrium indicating a neutral character for these compounds.

Complexation studies of compounds **1**–**6** with alkali and alkaline earth metal cations performed in dioxane–water system at wide range of pH values show no spectral changes. Thus, further experiments were performed under neutral conditions in pure acetonitrile. This solvent was chosen to enhance the stability of lithium complexes.[12] The neutral conditions for complexation studies are opposite to the previously described macrocyclic derivatives of *p*-alkylphenols and resorcinol that require strong basic conditions for alkali cation binding in dioxane–water solvent system. 18-Membered pyrrole compounds **1a** and **2a** form complexes with calcium, strontium and barium ions. 18-Membered pyrrole derivative (compound **1b**) forms complexes with most of the investigated metal cations and the values of the stability constants are rather high. Compound **1b** forms much stronger sodium complex than **2b**. 18-Membered derivative **3** forms complexes with alkaline earth metal cations while no significant changes in absorption spectra were observed in the presence of alkali metal cations. 21-Membered crown ether **4** is selective for potassium and barium cations; for the latter the spectral changes are more important and the complex stability constant log *K* is 4.59. Macrocyclic ether **5** containing an imidazole residue is selective for sodium cation among the alkali metal ions. The same compound forms complexes with alkaline earth cations of slightly differentiated stabilities. In all cases complexation occurs with significant color changes. The imidazole derivatives change color from red to yellow. Cation complexation by 2,5-substituted pyrroles is accompanied by color change from red to bluish. Less significant are color changes in the case of 2,3-substituted pyrroles. The stability constants for azole azocrown ether reagents 1:1 complexes, determined by spectrophotometric titration, are collected in Table 1.

Typical spectra of macrocyclic azole ligands and their changes in the presence of metal cations are presented in Figure 1.

Due to the neutrality of the chromogenic azole crown derivatives, they are prospective candidates for ion-carriers in ion-selective membrane electrodes. Potentiometric selectivity coefficients given as log $K^{Pot}_{M,X}$ (M=Na or K; X= interfering cation)[13] for mono- and divalent cations are collected in Tables 2 and 3. Electrodes containing pyrrole derivatives (**1b**, **2a**,**2b**, **4**) are potassium selective, however, membranes doped with 2,3-substituted pyrrole macrocycles (isomers **1b** and **2b**) possess better characteristics, for example the K/Na selectivity. No significant influence of the lipophilic alkyl substituent on selectivity increase was observed.[14] Electrodes containing imidazole derivatives **5** and **6** have quite good selectivity for sodium over potassium ((log $K^{Pot}_{Na,K}$=−1.77 for compound **5**). However, the electrodes were not stable for more than 2 weeks. The detection

Table 1. Stability constants for 1:1 crown ethers complexes of alkali and alkaline earth ions in acetonitrile (at 25°C)

Compound	log K_{Li}	log K_{Na}	log K_K	log K_{Mg}	log K_{Ca}	log K_{Sr}	log K_{Ba}
1a	[a]	[a]	[a]	[a]	3.50	3.71	2.54
1b	4.36	4.65	4.67	[a]	5.37	5.60	5.54
2a	[a]	[a]	[a]	[a]	2.60	3.54	1.54
2b	4.37	2.63	[a]	~2	5.68	5.46	4.30
3	[a]	[a]	[a]	4.46	5.47	5.92	4.46
4	[a]	[a]	~4	[a]	[a]	[a]	4.59
5	[a]	5.1	[a]	3.6	5.74	5.48	6.11
6	1.70	4.94	[b]	[b]	[b]	[b]	[b]

[a] No significant changes in UV–Vis spectra.
[b] Changes in spectra do not allow the determination of stability constants.

Table 2. Slopes S (mV) and selectivity coefficients[13] (log $K^{Pot}_{K,X}$) for membrane electrodes containing pyrrole compounds

Compound	S (mV)	log $K^{Pot}_{K,X}$ for X=								
		Li^+	Na^+	K^+	Rb^+	Cs^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
1b	57	−2.9	−2.9	0	−0.4	−1.8	−3.9	−3.6	−4.5	−4.2
2b	57	−2.6	−3.0	0	0.4	−1.6	−3.5	−3.8	−3.9	−3.8
2a	56	−1.4	−1.0	0	0.6	1.0	−2.6	−2.1	−2.0	−2.1

Table 3. Slopes S (mV) and selectivity coefficients[13] (log $K^{Pot}_{Na,X}$) for membrane electrodes containing imidazole compounds

Compound	S (mV)	log $K^{Pot}_{Na,X}$ for X=								
		Li^+	Na^+	K^+	Rb^+	Cs^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
5	58	−2.1	0	−1.5	−1.5	−2.0	−3.6	−3.0	−3.1	−1.0
6	55	−1.6	0	−1.2	−1.0	−1.5	−3.1	−2.6	−1.9	−0.3

limit (log LD) for electrodes with pyrrole derivatives is about −5.5 whereas, for imidazole derivatives it is −5.0. The slopes for potassium and sodium selective electrodes are in the range of 55–58 mV/decade (Tables 2 and 3).

Compound **1b** crystallized from methylene chloride–methanol (10:1) mixture afforded needle-like crystals with a molecule of methylene chloride, in a form suitable for X-ray analysis. The structure of this compound is shown in Figure 2. Both azo groups are *trans* with parameters similar to those found in the structure of 21-membered chromogenic azocrown ether derivative of *p*-cresol.[6] Both azo groups are *syn* to the pyrrole residue. The complexed methylene chloride molecule interacts by hydrogen bonds with the oxygen and nitrogen atoms of the macrocycle.

3. Conclusions

Chromogenic macrocyclic derivatives of azoles have been prepared in high yield. In the case of pyrrole compounds two positional isomers were recognized and characterized. In the case of imidazole crowns only one isomer was isolated. By UV–Vis spectroscopy it was found that in acetonitrile solution the reagents preferentially bind alkali or alkaline earth metal cations depending on the isomeric structure of the pyrrole macrocycle. Imidazole derivatives are selective towards sodium cations. Ion-selective membrane electrodes doped with pyrrole derivatives are potassium selective, whereas the respective imidazole compounds produce sodium selective electrodes.

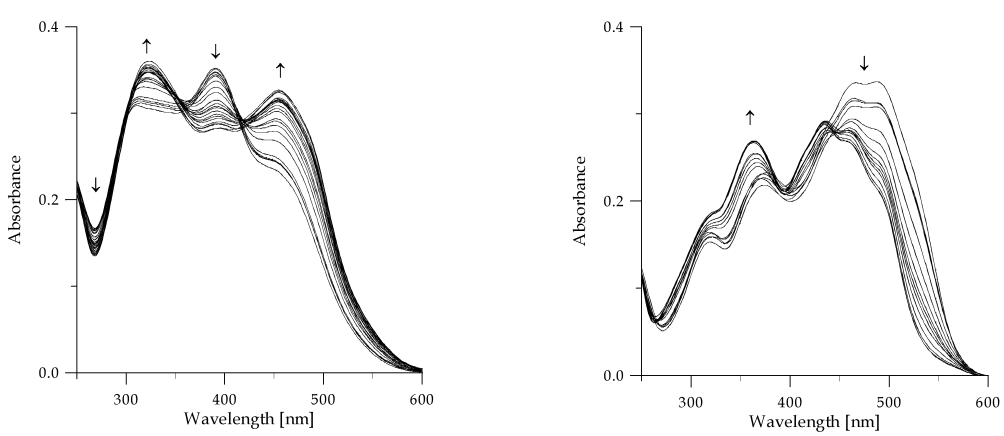

Figure 1. Absorption spectra of: (left) compound **1b** (c=1.8×10^{-5} M) and spectra in the presence of $LiClO_4$ (0–2.26×10^{-4} M); (right) compound **5** (c=1.64×10^{-5} M) and spectra in the presence of $NaClO_4$ (0–1.41×10^{-3} M) in acetonitrile under neutral conditions.

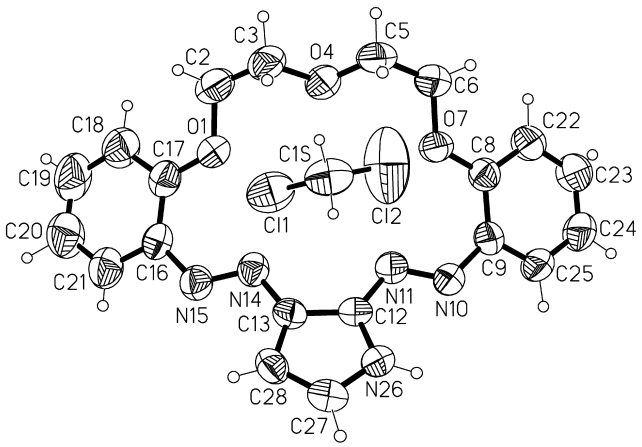

Figure 2. Structure of compound **1b** associated with methylene chloride.

4. Experimental

All materials and solvents were of analytical reagent grade. The starting diamines were prepared as described.[5,6,8] Aluminium plate covered with Silica gel 60 F_{254} (Merck) and methylene chloride–methanol (15:2 v/v) system were used for TLC chromatography. NMR spectra were recorded on Varian instruments. Mass spectra were taken on AMD-604 apparatus. UV–vis spectra were recorded on a Unicam UV-330 Spectrophotometer, IR spectra (film) on Genesis II (Mattson) instrument. Potentiometric measurements were done using 654 pH-meter (METROHM). As a reference OP-08201 Ag/AgCl electrode (Radelkis) was applied. The mp (°C) are uncorrected.

4.1. Syntheses

The syntheses were performed using a high dilution technique.

Two solutions were prepared:

Solution A. A suspension of respective bis-amine (2 mmol)[5,6] in 40 mL water was cooled in an ice-bath and acidified with conc. hydrochloric acid (1 mL). The clear solution was diazotized with sodium nitrite (0.28 g, 4.1 mmol) dissolved in 2 mL cold water.

Solution B. Pyrrole, imidazole or 1,2,4-triazole (2 mmol) and sodium hydroxide (0.2 g, 5 mmol) were dissolved in 40 mL water and ice cooled. In the case of pyrrole ethanol (2 mL) was added.

The above cold solutions A and B were dropped with the same speed during 45 min into 600 mL of vigorously stirred water (pH about 11 from NaOH). The temperature of the aqueous medium was kept at 10°C. Stirring at 10°C was continued for 1 h and then for 12 h at 25°C. The mixture was cooled to 0–5°C and pH was adjusted to 6–7 with acetic acid to precipitate the crude products.

Crown ethers were isolated from the collected solid material using column chromatography. Compounds **1** and **2** were isolated using chloroform as the initial eluent, then chloroform–acetone (4:1), and finally chloroform–methanol (15:2) mixture. As an eluent, methylene chloride was used in the case of compound **3**, and chloroform for compounds **4**–**6**.

Use of sodium or potassium nitrite to generate diazonium salts, and sodium or potassium hydroxide to maintain pH at the coupling stage does not influence the yield of macrocyclic products.

No macrocyclic product was identified when 1,2,4-triazole was reacted with bis-diazonium salts under different conditions.

4.1.1. Compound 1a. Yield 25%, red solid, mp 204–208°C. R_f~0.8. ^{1}H NMR; δ_H ($CDCl_3$; 500 MHz): 10.45 (~1H, s, N*H*); 7.82 (2H, d, *J*=8.3 Hz, Ar*H*); 7.42–7.36 (2H, m, Ar*H*); 7.14–7.06 (6H, m, Ar*H*); 4.42–4.38 (4H, m, ArOCH_2); 4.04–4.00 (4H, m, CH_2OCH_2). ^{13}C NMR; δ_C ($CDCl_3$; 125 MHz): 70.95; 71.29; 116.02; 116.52; 117.39; 122.71; 132.69; 142.96; 147.44; 157.19. IR ν_{max} (film): 3435; 2931; 2870; 1586; 1485; 1446; 1374; 1276; 1119; 1029; 751. UV–Vis (acetonitrile): λ_1=252 nm, ε_1=4.86×10^3; λ_2=312 nm, ε_2=6.81×10^3; λ_3=374 nm, ε_3=7.10×10^3; λ_4=506 nm, ε_4=1.29×10^4. HRMS (EI): M^+ 377.1491; $C_{20}H_{19}N_5O_3$ requires 377.1488.

4.1.2. Compound 1b. Yield 23%, deep orange solid, mp 90–92°C. R_f~0.4. ^{1}H NMR; δ_H ($CDCl_3$; 500 MHz): 9.28 (~1H, s, N*H*); 7.74 (1H, dd, J_1=1.7 Hz, J_2=8.1 Hz, Ar*H*); 7.65 (1H, dd, J_1=1.7 Hz, J_2=7.7 Hz, Ar*H*); 7.24–7.32 (2H, m, Ar*H*+*CDCl*$_3$); 7.07–7.14 (2H, m, Ar*H*); 7.0 (2H, d, *J*=8.1 Hz, Ar*H*); 6.91 (1H, s, Ar*H*); 6.68 (1H, s, Ar*H*); 4.10–4.20 (4H, m, ArOCH_2); 4.00–3.85 (4H, m, CH_2OCH_2). ^{13}C NMR; δ_C ($CDCl_3$; 125 MHz): 69.18; 69.89; 99.68; 114.33; 114.56; 121.42; 130.30; 130.56; 130.94; 142.52; 142.76; 149.45. IR ν_{max} (film): 3420; 3145; 3068; 2924; 2855; 1594; 1574; 1485; 1449; 1363; 1273; 1239; 1119; 1086; 1063; 928; 751; 561. UV–Vis: (acetonitrile): λ_1=245 nm, ε_1=1.12×10^4; λ_2=311 nm, ε_2=1.54×10^4; λ_3=391 nm, ε_3=1.72×10^4; λ_4=460 nm, ε_4=1.12×10^3. HRMS (EI): M^+ 377.1490; $C_{20}H_{19}N_5O_3$ requires 377.1488.

4.1.3. Compound 2a. Yield 27%, red solid, mp 176°C. R_f~0.8. ^{1}H NMR; δ_H (d_6-acetone, 200 MHz): 10.46 (~1H, s, N*H*); 7.82 (2H, d, *J*=2.5 Hz, Ar*H*); 7.54 (2H, dd, J_1=2.5 Hz, J_2=8.8 Hz, Ar*H*); 7.17 (2H, d; *J*=8.8 Hz, Ar*H*) 7.12 (2H, s, Ar*H*); 4.40–4.30 (4H, m, ArOCH_2); 4.10–4.00 (4H, m, CH_2OCH_2); 1.4 (18H, s, Ar-*t-Bu*). IR ν_{max} (film): 3432; 2925; 2868; 1498; 1454; 1364; 1289; 1264; 1185; 1162; 1066; 1027; 756. UV–Vis (acetonitrile): λ_1=250 nm, ε_1=4.43×10^3; λ_2=314 nm, ε_2=5.61×10^3; λ_3=388 nm, ε_3=5.49×10^3; λ_4=518 nm, ε_4=1.28×10^4. HRMS (EI): M^+ 489.2755; $C_{28}H_{35}N_5O_3$ requires 489.2740.

4.1.4. Compound 2b. Yield 11%, deep orange solid, mp 160°C (decomposition). R_f~0.3. ^{1}H NMR; δ_H ($CDCl_3$, 500 MHz): 9.40 (~1H, s, N*H*); 7.60 (1H, s, Ar*H*); 7.40 (1H, s, Ar*H*); ~7.30 (2H, m, Ar*H*+*CDCl*$_3$) 6.59 (2H, d, *J*=8.3 Hz, Ar*H*); 6.58 (1H, s, Ar*H*); 6.54 (1H, s, Ar*H*); 4.30 (4H, s, ArOCH_2); 3.95 (4H, s, ArOCH$_2$CH_2); 1.4 (18H, s, Ar-*t-Bu*). IR ν_{max} (film): 3399; 3166; 2926; 2869; 1498;

1456; 1364; 1263; 1132. UV–Vis (acetonitrile): λ_1=247 nm, ε_1=5.90×10^3; λ_2=314 nm, ε_2=7.39×10^3; λ_3=396 nm, ε_3=7.55×10^3; λ_4=518 nm, ε_4=6.70×10^3. HRMS (EI): M^+ 489.2757; $C_{28}H_{35}N_5O_3$ requires 489.2740.

4.1.5. Compound 3. Yield 27%, red solid, mp 105–108°C. R_f~0.7. ^{1}H NMR δ_H (d_6-acetone, 500 MHz): 10.80 (1H, s, N*H*); 7.66 (2H, d, *J*=1.8 Hz, Ar*H*); 7.26 (2H, dd, J_1=2.6 Hz, J_2=8.4 Hz, Ar*H*); 7.08 (2H, s, Ar*H*); 7.05 (2H, d, *J*=8.4 Hz, Ar*H*); 4.34–4.38 (4H, m, ArOCH_2); 3.97–4.20 (4H, m, CH_2OCH_2); 3.62 (4H, t, *J*=7.0 Hz, ArCH$_2$CH_2); 3.36 (6H, s, OCH_3); 2.88 (4H, t, *J*=7.0 Hz, ArCH_2CH_2). IR ν_{max} (film): 3433; 2924; 2871; 2360; 2341; 1573; 1498; 1454; 1374; 1233; 1158; 1112; 1065; 1029; 805; 669. UV–Vis (acetonitrile): λ_1=250 nm, ε_1=8.51×10^4; λ_2=314 nm, ε_2=1.10×10^5; λ_3=388 nm, ε_3=1.08×10^5; λ_4=518 nm, ε_4=2.40×10^5. HRMS (EI): M^+ 493.2301; $C_{26}H_{31}N_5O_5$ requires 493.2325.

4.1.6. Compound 4. Yield 41%, red solid, mp 156–157°C. R_f~0.8. ^{1}H NMR; δ_H ($CDCl_3$, 200 MHz): 12.6 (1H, s, N*H*); 7.54–7.82 (2H, m, Ar*H*); 7.26–7.39 (2H, m, Ar*H*); 6.97–7.06 (6H, m, Ar*H*); 4.33–4.26 (4H, m, ArOCH_2); 3.91–3.97 (4H, m, ArOCH$_2$CH_2); 3.82 (4H, s, OCH_2CH_2O). IR ν_{max} (film): 3589; 3496; 3010; 2918; 1587; 1486; 1450; 1388; 1277; 1249; 1161; 1110; 1056; 950; 843; 752; 667; 613; 596; 555; 483. UV–Vis (acetonitrile): λ_1=250 nm, ε_1=6.53×10^3; λ_2=311 nm, ε_2=7.10×10^3; λ_3=372 nm, ε_3=7.46×10^3; λ_4=494 nm, ε_4=2.40×10^4. HRMS (EI): M^+ 421.1737; $C_{22}H_{23}N_5O_4$ requires 421.1750.

4.1.7. Compound 5. Yield 42%, red solid, mp 228–232°C. R_f~0.5. ^{1}H NMR; δ_H ($CDCl_3$, 200 MHz): 8.1 (1H, s, Ar*H*); 7.85 (1H, d, *J*=8.1 Hz, Ar*H*); 7.60 (1H, d, *J*=8.3 Hz, Ar*H*); 7.38–7.51 (2H, m, Ar*H*); 7.00–7.20 (4H, m, Ar*H*); 4.35–4.50 (4H, m, ArOCH_2); 3.80–4.10 (4H, m, CH_2OCH_2). ^{13}C NMR; δ_C ($CDCl_3$; 125 MHz): 71.17; 71.24; 116.07; 116.55; 117.71; 117.85; 122.95; 133.76; 135.36; 142.47; 142.70; 146.16; 155.18; 157.60; 158.37. IR ν_{max} (film): 3567; 3513; 3435; 2928; 2878; 1589; 1530; 1486; 1448; 1281; 1234; 1159; 1112; 1064; 1039; 940; 754; 670; 604; 557; 480; 426. UV–Vis (acetonitrile): λ_1=241 nm, ε_1=8.97×10^3; λ_2=317 nm, ε_2=1.01×10^4; λ_3=376 nm, ε_3=1.38×10^4; λ_4=469 nm, ε_4=1.95×10^3; λ_5=486 nm, ε_5=1.95×10^4. HRMS (EI): M^+ 378.1446; $C_{19}H_{18}N_6O_3$ requires 378.1440.

4.1.8. Compound 6. Yield 30%, red solid, mp 223°C. R_f~0.6. ^{1}H NMR; δ_H ($CDCl_3$, 200 MHz): 11.4 (1H, s, N*H*); 8.10 (1H, s, Ar*H*); 8.0 (1H, d, *J*=2.4 Hz, Ar*H*); 7.85 (1H, d, *J*=2.2 Hz, Ar*H*); 7.62–7.48 (2H, m, Ar*H*); 7.18–7.06 (4H, m, Ar*H*); 4.46–4.34 (4H, m, ArOCH_2); 4.08–3.94 (4H, m, CH_2OCH_2); 1.4 (18H, s, Ar-*t-Bu*). IR ν_{max} (film): 3572; 3517; 3427; 2960; 1499; 1460; 1363; 1264; 1232; 1188; 1124; 1065; 812; 754. UV–Vis (acetonitrile): λ_1=330 nm, ε_1=4.61×10^3; λ_2=382 nm, ε_2=5.99×10^3; λ_3=490 nm, ε_3=6.98×10^3. HRMS (EI): M^+ 490.2684; $C_{27}H_{34}N_6O_3$ requires 490.2692.

4.2. Determination of stability constants

Stability constants of azole crown ether complexes with alkali and alkaline earth cations were determined by spectrophotometric titrations. The spectra were recorded up to high excess of cation to crown ether and finally the limiting spectra were obtained. The dependence of the absorbance on metal salt concentration was described well by equation $(A_0-A)/(A-A_i)=K[M^+]$[15] where A_0 and A_i are the absorbancies at zero and infinite salt concentration, respectively. Data taken at least at three different wavelengths were fitted to the above equation.

4.3. Membrane preparation and emf measurements

The membrane components [5 mg of crown ether, 50 mg PVC, 0.1 mL 2-nitrophenyl octyl ether and 1 mg potassium tetrakis(4-chlorophenyl)borate] were dissolved in 1 mL freshly distilled THF and poured into a 2 cm diameter glass ring. After solvent evaporation, the membranes were incorporated into Ag/AgCl electrode bodies. 0.01 M NaCl was used as internal electrolyte. Selectivity coefficients were determined by separate solution method (SSM) at 10^{-2} M activity of metal chlorides.[13]

4.4. Supplementary data

Supplementary data are deposited with the Cambridge Crystallographic Data Centre as a supplementary publication numbers CCDC 203525 (CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK; e-mail; deposit@ccdc.cam.ac.uk).

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References

1. Kaneda, T.; Sugihara, K.; Kanuiga, H.; Misumi, S. *Tetrahedron Lett.* **1981**, *22*, 4407–4408.
2. Nakashima, K.; Nakatusi, S.; Akiyama, S.; Kaneda, T.; Misumi, S. *Chem. Lett.* **1982**, 1781–1782.
3. Dix, J. P.; Vögtle, F. *Chem. Ber.* **1981**, *114*, 638–651.
4. Loehr, H. G.; Vögtle, F. *Acc. Chem. Res.* **1985**, *18*, 65–72.
5. Skwierawska, A.; Inerowicz, H. D.; Biernat, J. F. *Tetrahedron Lett.* **1998**, *39*, 3057–3060.
6. Wagner-Wysiecka, E.; Skwierawska, A.; Kravtsov, V. Ch.; Biernat, J. F. *J. Supramol. Chem.* **2001**, *1*, 77–85.
7. Sultanov, A. V.; Savvin, S. B. *Khimia Geterocycl. Soed. Russ.* **1988**, 126–130.
8. Wagner-Wysiecka, E.; Luboch, E.; Marczak, B.; Biernat, J. F. *Polym. J. Chem.* **2001**, *75*, 1457–1464.
9. Inerowicz, H. D. *J. Incl. Phenom.* **2001**, *39*, 211–214.

10. Wagner-Wysiecka, E.; Luboch, E.; Biernat, J. F. *J. Incl. Phenom.* **2001**, *4*, 19–22.
11. Luboch, E.; Bilewicz, R.; Kowalczyk, M.; Wagner-Wysiecka, E.; Biernat, J. F. *Advances in Supramolecular Chemistry: Azo Macrocyclic Compounds*; **2003**; *9*, 73–163.
12. Okada, T.; Quraishi, S. B. *Phys. Chem. Chem. Phys.* **2000**, *2*, 5624–5629.
13. Umezawa, Y.; Bühlmann, P.; Umezawa, K.; Thoda, K.; Amemiya, S. *Pure Appl. Chem.* **2000**, *72*, 1851–2082.
14. Luboch, E.; Biernat, J. F.; Simonov, Yu. A.; Kravtsov, V. Ch.; Bel'skii, V. K. *Supramol. Chem.* **1999**, *11*, 109–118.
15. Goldenberg, L. M.; Biernat, J. F.; Petty, M. C. *Langmuir* **1998**, *14*, 1236–1241.