



Chromoionophores with Chromophores as Integral Part(s) of the Macrocycle in Crown Ethers

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Abstract

Several new types of ionizable chromoionophores have been synthesized. Their reactions with metal cations have been studied by spectroscopic methods. Preferential complexation of lithium ions was found for many of these reagents.

Introduction

Chromoionophores are reagents changing color or fluorescence upon interaction with ions [1–4]. They consist of a crown ether residue and a chromophore unit usually located in a side arm. Proton-dissociable chromogenic crown ethers [5–9], typically phenol derivatives, abstract protons to form anionic species of higher affinity to metal cations. However, spectral separations between the parent ligands, the ‘free’ anions and their complexes are generally small (10–30 nm) when complexation with different alkali metal ions is concerned.

The troublesome inconvenience of chromoionophore properties could be overcome by: applying a solvent in which some salts are selectively soluble [1–3]; by improving the cation discrimination according to its size [10, 11]; or by altering the arrangement of the chromophore unit to make it more sensitive for cation interaction within the chromoionophore cavity.

The last approach, previously announced by us [12–14], consists in changing the location of the chromophore unit. Previously, we described new proton-dissociable crown compounds **1–6** resembling mordant azo dyes. They comprise the same assemblage of structural elements typical for various metallochromic reagents, and a cation size controlling macrocyclic site. The location of the azo groups enables their direct interaction with the complexed cation. It was expected that cations in complexes may coordinate to the phenolate anion, to the electron donating polyether oxygen atoms of the macrocycle and to one of the nitrogen atoms of each azo group (cf., for example [15]) of the chromophore. In turn, the structures should cause significant spectral differences between the chromogenic compound and its complex. A similar behavior was expected for derivatives of resorcinol, pyrrole, imidazole and azocrowns with peripheral phenolic OH groups.

p-Alkylphenol chromoionophores

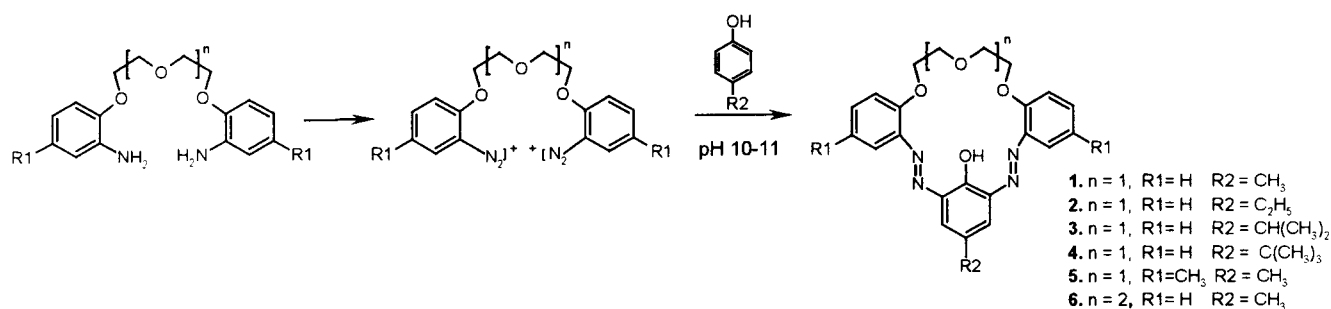
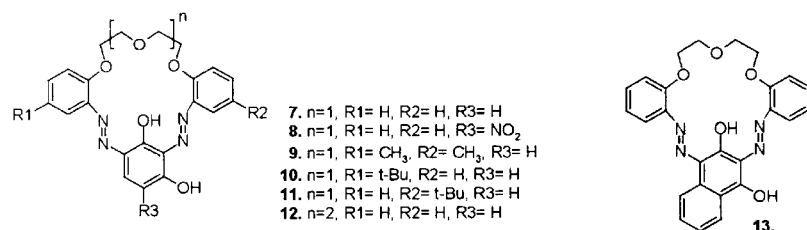
Synthesis of compounds **1–6** [12, 14] was performed as shown in Scheme 1. The respective diamines [16–18] were diazotized and coupled with *p*-substituted phenols.

The obtained crown ethers comprise weak acidic OH and weak basic –N=N– centers. In acidic medium, in mixed water-dioxane (1 : 1) solvent the green color is caused by protonation of the azo group. The pK_a constant for compound **2** is 3.02. Under basic conditions (R_4NOH) significant color changes are observed just at 1 molar concentration of base. The unusual acid-base properties of the crown ethers were attributed to the intramolecular hydrogen bond of the OH group with the –N=N– residue, as observed from crystal structures and large shifts of OH protons in 1H NMR [14]. In solutions, the OH protons in compounds **1–6** occupy two equivalent positions forming hydrogen bonds with one or with the another azo group. It formally corresponds to rotation of the OH group. Thermodynamic parameters of the rotation established by low temperature 1H NMR studies are: the constant rate k_c at coalescence temperature (188 K) is $83 s^{-1}$ and the free activation energy ΔG^\ddagger equals $35 kJ \cdot mol^{-1}$, cf., [14, 19].

Brownish solutions of **1–6** in pure dioxane at slightly basic conditions turned to pink upon adding lithium acetate. The selectivity of this reaction could be attributed to the solubility of only lithium salts in the used solvent, cf. [1–3, 20]. This reaction could be used to detect even small amount of lithium cations [20].

Absorption spectra of azocrown ether **1** in water-dioxane (1 : 1 v/v; pH adjusted to about 12 with Et_4NOH) show $\lambda_{max} = 332 nm$, ($\epsilon_{max} = 2.15 \times 10^4$); there is no absorption maximum at about 500 nm. In the presence of lithium chloride a new band appears at $\lambda_{max} = 525 nm$ (isosbestic point 463 nm). The stability constant for the 1 : 1 complex $\log K_{Li}$ is 2.95. For sodium and potassium the new bands are at $\sim 560 nm$. The stability constants are $\log K_{Na} = 2.51$ and $\log K_K = 1.92$, respectively [12]. The behavior of compounds **2–5**

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Scheme 1. Synthesis of *p*-alkylphenol derivative chromogenic azocrown ethers 1–6.

Scheme 2. Synthesized resorcinol derived chromogenic azocrown ethers 7–13.

is similar. The spectral separation between the lithium and sodium, and the lithium and potassium complexes is about 35 nm. For 21-membered compound **6** the log K values for lithium, sodium and potassium complexes are 2.36, 2.09 and 1.71, respectively [20].

Compounds **1–6**, show no spectral changes on addition of ammonium or guanidinium salts. Interestingly, many studied cations do not interfere with lithium, sodium or potassium under the described conditions due to insolubility of their hydroxides. This concerns also other small cations like beryllium, aluminium or lanthanum.

Resorcinol chromoionophores

Macrocyclic derivatives of resorcinol, first prepared by Sultanov and Savvin [18], in many respects resemble the above *p*-alkylphenol crowns. The synthesis of macrocyclic derivatives of resorcinol **7–13** was carried out under the conditions described for *p*-alkylphenol chromoionophores [12, 14] (Scheme 2 [13]). Contrary to rather moderate yields of macrocycles **1–6** (average 20%) the yield of compounds **7–12** obtained by coupling resorcinol with diazonium salts under high dilution conditions [13] is around 50% in accordance with the yield for compound **7** given by Sultanov [18]. For dihydroxynaphthalene chromoionophore **13** the yield is 11%.

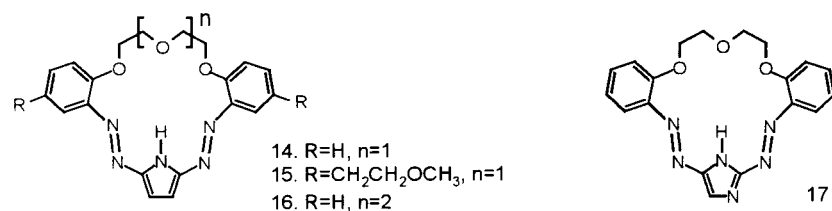
These compounds also comprise weak acidic OH and weak basic $-N=N-$ centers. In water-dioxane (1 : 1) system in acidic medium neither color nor spectral changes were observed. In basic solutions changes are observed at extremely high pH(s) (1M Me₄NOH). For 4-nitroresorcinol derivative **8** color and spectral changes are observed at pH about 9 (calculated pK_a is 12.9; water-dioxane system) [13]. Table 1 collects parameters of the absorption bands and stability constants for alkali metal complexes with resorcinol crowns.

Table 1. Absorption bands for compounds **7–13** (water-dioxane 1 : 1 solvent system; pH 12) and stability constants for their lithium and sodium complexes

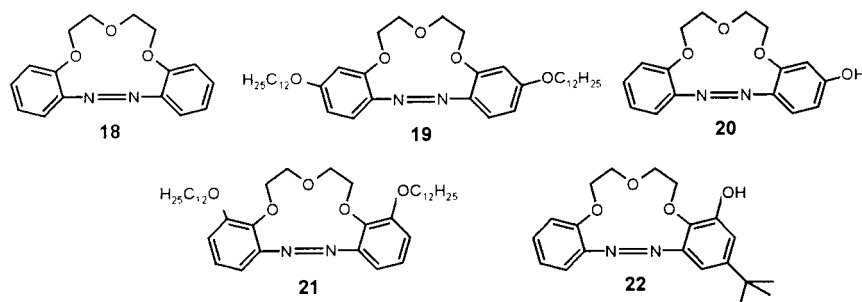
Compound	λ_{max} [nm]	ϵ_{max}	log K_{Li} (isosbestic point)
7	434	3.02×10^4	3.79 (516)
8*	356	1.03×10^5	3.52 (449)
9	441	1.12×10^4	3.96 (525)
10	438	2.95×10^4	
11	436	3.84×10^4	
13	237, 264 434, 550	7.60×10^3 , 1.66×10^4 1.74×10^4 , 7.40×10^3	3.36 (530)
			log K_{Na} (isosbestic point)
12	421	3.78×10^4	3.28 (505)

*Measured at pH 9.

Resorcinol crown ethers **7–13** form complexes with alkali metal ions in strongly basic solution (pH \approx 12). Complexation of compound **8** was studied at pH \approx 9. Compounds **7–11** ($n = 1$) are selective reagents for lithium ions. Interesting are the spectral properties of naphthocrown **13**. This crown shows four bands in the UV-vis spectrum (Table 1). In this case the complexation process is easier to observe because the absorption at 550 nm extensively decreases and the absorption at about 500 nm increases upon addition of lithium salts. In the presence of sodium ions negligible spectral changes are observed for 18-membered resorcinol derivatives **7–11** and for compound **13**. For 21-membered crown ether **12** the most noticeable changes were found in the presence of sodium cations (Table 1). Spectral changes in the presence of potassium ions are not observed neither for 18-membered nor for 21-membered crown ethers.



Scheme 3. Azocrown ether derivatives of pyrrole and imidazole.



Scheme 4. Structures of compounds 18–22.

Table 2. Stability constants for alkali and alkaline earth metal complexes of compounds 14–17 in acetonitrile

Compound	log K_{Li}	log K_{Na}	log K_{K}	log K_{Mg}	log K_{Ca}	log K_{Ba}
14	4.36	4.65	4.67	*	5.37	5.54
15	*	*	*	4.46	5.27	4.46
16	*	*	*	*	*	4.59
17	*	5.1	≈4	3.6	5.74	6.11

*Indicates no changes in absorption spectra.

Azole chromoionophores

In compounds 14–17 (Scheme 3) the residue of resorcinol is replaced by an azole unit. They were obtained by coupling the above diazonium salts with pyrrole or imidazole.

Under neutral conditions in acetonitrile compound 14 forms complexes with lithium, sodium and potassium. However, the most distinctive spectral changes are with lithium ions. Compound 17 forms complexes with sodium and potassium. In this case lithium causes no spectral changes. Crowns 14–17 form complexes with some alkaline earth cations (Table 2).

Chromoionophores with peripheral OH or OR group

Other studied compounds are azocrown ethers 19–22 (Scheme 4), derivatives of the parent azocrown ether 18 [21, 22]. The synthesis of compound 20 is exemplified in Scheme 5.

Compounds 18–22 preferentially bind lithium cations among alkali metal cations. Some of them bind also alkaline earth metal cations. The stability constants are collected in Table 3.

For compounds 18–22 complexation was studied in neutral medium and for compounds 20 and 22 additionally at

Table 3. Stability constants for cation complexes of compounds 18–22 in acetonitrile

Compound	log K_{Li}	log K_{Na}	log K_{K}	log K_{Mg}	log K_{Ca}	log K_{Ba}
18	4.29 (4.10) [21]	– [21]	*	*	*	*
19	4.31	*	*	*	*	*
20	3.23 (pH ≈ 9)	*	*	3.30	4.21	3.0
21	3.43	*	*			
22	4.20	*	*			

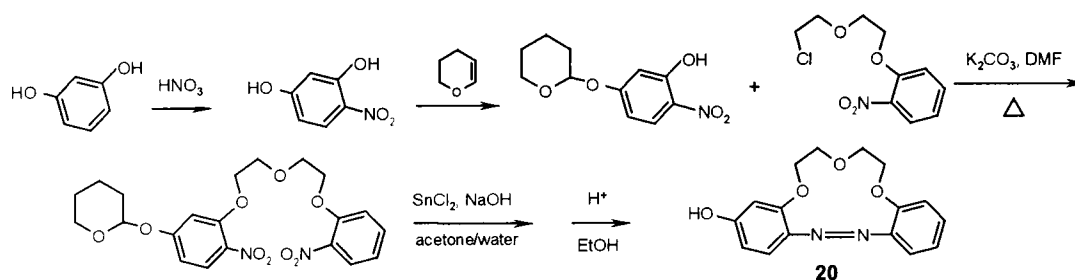
*Indicates no significant changes in spectra.

pH(s) ≈ 9. The most significant spectral changes are for 20, 22 and 19 in the given order. For the lithium complex with 19 an additional band appears, whereas complex formation with 20 and 22 is well recognizable due to a significant shift of bands of the ligand and its lithium complex. No observable spectral changes for 20 are found in the presence of sodium cations.

Conclusions

New chromogenic reagents are prepared. The chromoionophores combine a proton dissociable unit and one or two azo groups in such a way that they form inherent parts of the crown macrocycle. As proton dissociable groups phenolic OH and azole NH were chosen.

Some of the chromoionophores are valuable for recognition of lithium cations with large separations of spectral bands for the ligands and their complexes (up to 150 nm), and moderate spectral differentiation between lithium and sodium complexes. Some of these reagents require strongly basic conditions and mixed aqueous–organic solvents. Azole



Scheme 5. Synthesis of compound 20.

chromoionophores react with metal cations in neutral or slightly basic acetonitrile.

The 13-membered azocrown with a peripheral phenolic group preferentially forms a lithium complex in acetonitrile under slightly basic conditions with satisfactory spectral separations.

Comparing properties of the chromoionophores derivatives of *p*-alkylphenol, resorcinol and azoles it can be concluded that compounds in which the number of azo groups exceeds the number of phenolic groups are better metallochromic reagents since the spectral separations for the ligand and the respective complexes are larger.

Acknowledgements

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