Tetrahedron 65 (2009) 10671–10678

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

4-Hexylresorcinol-derived hydroxyazobenzocrown ethers as chromoionophores

Elżbieta Luboch *, Ewa Wagner-Wysiecka, Tomasz Rzymowski

Department of Chemical Technology, Chemical Faculty, Gdansk University of Technology, Narutowicza 11/12, 80-233 Gdańsk, Poland

ARTICLE INFO

Article history:
Received 6 July 2009
Received in revised form
1 October 2009
Accepted 15 October 2009
Available online 20 October 2009

Keywords:
Azobenzocrown ethers
Williamson reaction
Hydroxyazobenzene ⇄ quinone-hydrazone tautomerism
Metal cation complexation
UV–vis spectroscopy
Colorimetric assays
Chromoionophores

ABSTRACT

The synthesis of novel chromoionophoric azobenzocrowns with a hydroxyl group in the *para* position to the azo moiety has been described. The interactions of the obtained colored macrocycles with selected alkali and alkaline earth metal cations were investigated in acetonitrile by UV–vis spectroscopy.

1. Introduction

Crown ethers incorporating an azobenzene residue as part of the macrocycle are interesting metal complexing reagents.[1] Macrocycles with inherent 2,2′-azobenzene[2–4] or 4,4′-azobenzene[5] residues were obtained and investigated. A set of macrocycles containing an azophenol residue was also obtained. Incorporation of an azophenol residue leads to chromoionophores belonging to proton dissociable (anionic) compounds. These chromoionophores possess either a peripheral azo unit with an OH group directed into the cavity,[6] or a –N=N– group constituting part of the macrocycle.[7–11] In the last case, the phenolic OH is, in most cases, located on the molecule periphery cf.[7–9] or is directed inside the macrocycle as in the case of *p*-alkylphenol derivatives.[10] There are also known resorcinol derivatives,[11] in which one OH group is directed inside the cavity and the another outside.

Complexation of cations by azophenol derivatives of macrocyclic compounds is favored under basic conditions, because the interaction of anionic species formed upon proton abstraction with cations is stronger. Azophenolic crown ethers with an OH group directed inside the cavity require less basic conditions to replace the proton by the cation due to competition. This effect is well documented, and the cavity–cation diameter fit plays an important role. Numerous chromoionophores belonging to this type were found to selectively interact especially with lithium cations in organic solvents.[6d] Cram's spherand[12] also selectively binds lithium cations in dioxane-water solution, but the complexation process is very slow. For phenol crown ethers with two inherent azo units, lithium complexation in dioxane-water proceeds with the spectroscopic inherent time scale.[10] Application of a mixed solvent system is convenient from a practical point of view, because for lithium determination, an aqueous sample should only be diluted with dioxane. Nitro and dinitro derivatives of phenylazophenol crown ethers were also studied with special emphasis to the spectroscopic separations of bands for free ligands and their complexes.[1]

For *para* or *ortho* hydroxyazobenzenes, tautomerization to the quinone-hydrazone form is known to occur.[13] The physical properties of azo dyes (e.g., color) are closely related to this tautomerism. In their UV–vis spectrum, the absorption maximum of the hydrazone form is typically shifted toward longer wavelength values in relation to the azo form.[14] In the solid state, *o*- and *p*-hydroxyazobenzenes exist mainly in the azo form, whereas naphthalene derivatives are in the hydrazone form or as a mixture of both hydrazone and azo form. The tautomeric equilibrium is affected by a solvent. In general, the hydrazone form is favored in more polar solvents.[15,16]

Tautomerization studies of 4-(4′-substituted-phenylazo)-1-naphthols[17] by Kishimoto showed that electron donating substituents in the *para* position to the azo unit stabilize the azo form

---

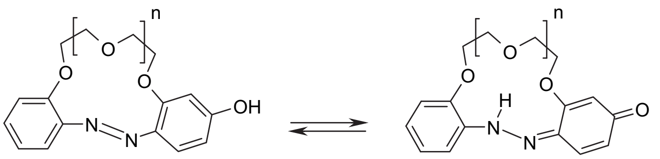
* Corresponding author. Tel.: +48 58 347 1759; fax: +48 58 347 1949.
E-mail address: elub@chem.pg.gda.pl (E. Luboch).

0040-4020/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2009.10.054

while electron accepting groups stabilize the hydrazone form. The equilibrium depends on solvent; in DMSO and DMF, the compounds exist in dissociated form.

The phenylazophenol⇄quinone-phenylhydrazone tautomerization also occurs in the case of macrocyclic azophenol chromoionophores, cf.[6a]

It was stated that macrocyclic *p*-hydroxyazobenzene derivative - compound **1** (Fig. 1), with an inherent azo unit, in the solid state[18] and in solvents of different polarity (chloroform, acetonitrile, acetone, or methanol) exists in the quinone-hydrazone form. The azophenol form was observed (∼30%) only in DMSO.[7] The quinone-hydrazone form is stabilized in this case by hydrogen bonds inside the cavity (Fig. 2).



1 n = 1
2 n = 2
3 n = 3

Figure 1. Tautomeric equilibrium for hydroxyazobenzocrown ethers.

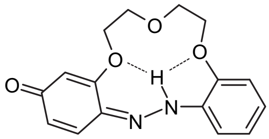


Figure 2. Hydrogen bonds inside the cavity of azobenzocrown **1**.

It was found that the tautomerization equilibrium is affected by the size of the macrocycle; the larger the cavity size the lower the tendency to exist in the quinone-hydrazone form probably due to weaker hydrogen bonds. Compound **2** (Fig. 1) in chloroform and in acetonitrile exists, like **1**, in the quinone-hydrazone form, but in DMSO only the azophenol form was found. 19-Membered compound **3** exclusively exists in the azophenol form, e.g., in DMSO and chloroform, while in acetonitrile the abundance of this form is no less than 75%.[8]

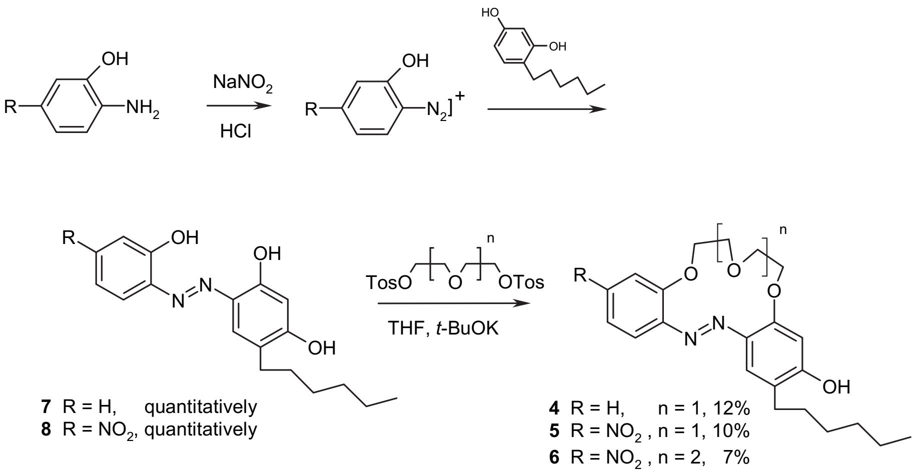
The ^{1}H NMR and UV–vis spectroscopic studies of compounds **1**–**3** were carried out to examine the influence of metal cation complexation on the tautomeric equilibrium.[6,7] The ^{1}H NMR spectra shows that compound **1** in pure acetonitrile and upon addition of the weak base, triethylamine, exists in the quinone-hydrazone form. However, in acetonitrile and in the absence of base, lithium perchlorate forms complexes with both tautomers. Addition of triethylamine to this mixture shifts the equilibrium toward one complex, probably the ionized ligand.

This paper presents a simple method for the synthesis of new 13- and 16-membered azobenzocrown ethers, with an inherent azo unit and with a hydroxyl group in the *para* position to it, i.e., derivatives of 4-hexylresorcinol. In addition, a nitro group was introduced to the benzene residue without the hydroxyl substituent. For the synthesized compounds, spectroscopic properties and interaction studies with metal cations important from a biological or medicinal point of view were carried out. The 4-hexylresorcinol building block was chosen to study the synthetic effect of an *o*-alkyl residue to the OH group, and the NO_2 group was chosen to study the effect of an electron accepting group on cation complexation and spectroscopic properties e.g., the position of absorption band maximum.

2. Results and discussion

2.1. Synthesis

Azobenzocrown ethers **1**–**3** were previously obtained in multistep reactions including reductive macrocyclization of the respective dinitropodands[7,8] with sodium stannite (Na_2SnO_2) in acetone/water mixture. Alternatively, hydroxyazomacrocycles may be synthesized in a reaction analogous to a Wallach rearrangement.[9] Attempts to obtain the above hydroxyazobenzocrowns (**1**–**3**) by Williamson reaction of the 2,2′-dihydroxyazobenzene with ditosylates as the last step formed only traces of crowns from the reaction mixture, in which polymeric products dominated. In contrast to the above completely ineffective synthesis, the Williamson reaction of 5-*n*-hexyl-2,2′,4-trihydroxyazobenzene with 1,7-ditosyl-1,4,7-trioxaheptane yielded 12% of 13-membered crown **4**. Analogously, reaction of 5-*n*-hexyl-2,2′,4-trihydroxy-4′-nitro-azobenzene with the same ditosyl derivative or 1,10-ditosyl-1,4,7,10-tetraoxadecane produces 13- and 16-membered nitro crowns **5** and **6** with 10 and 7% yield, respectively. The more favored cyclization reaction course of the hexyl substituted substrate than in the case of the 2,2′-dihydroxyazobenzene could be attributed to the presence of the hexyl group that sterically hinders alkylation of the adjacent resorcinol OH group. The synthesis of functionalized azobenzocrown ethers **4**, **5**, and **6** is shown in Scheme 1. In such solvents as: chloroform, DMSO, methanol, acetone or acetonitrile compound **5** exists in the quinone-hydrazone form.



7 R = H, quantitatively
8 R = NO_2, quantitatively

4 R = H, n = 1, 12%
5 R = NO_2 , n = 1, 10%
6 R = NO_2 , n = 2, 7%

Scheme 1. The synthesis of azobenzocrown ethers with peripheral hydroxyl group—derivatives of 4-hexylresorcinol.

2.2. Spectroscopy: interaction with metal cations

Metal cation complexation properties of crowns **4**–**6** were investigated by UV–vis and ^{1}H NMR spectroscopy, in neutral acetonitrile (in acetonitrile compounds **4**–**6** exist in the quinone-hydrazone form) and in acetonitrile containing triethylamine. The influence of concentrations of triethylamine on spectroscopic changes was studied using UV–vis spectroscopy. ^{1}H NMR spectroscopy allowed the azo-hydrazone equilibrium tracing and studies of interactions with metal cations, however in a narrow range of concentrations of amine and metal salts.

In the absence of the organic base in the UV–vis spectra of compound **4**, no noticeable changes were observed in the presence of alkali metal perchlorates. Similarly, no significant influence of triethylamine concentration on the location or intensity of the absorption band of the ligand in the UV–vis spectra was found. However, it was found that compound **4**, in acetonitrile, selectively binds a lithium cation in the presence of sodium and potassium cations upon addition of triethylamine.

To establish the optimal amount of triethylamine, spectra in the presence of 500-fold excess of lithium perchlorate (amount enabling achievement of the limiting spectrum) and different amounts of triethylamine were registered. It was found that addition of about 14,000-fold excess of triethylamine to crown (mol/mol), results in the best band separation. Under these conditions the value of the stability constant of the lithium complex with ligand **4**, log $K_{\mathrm{Li}}\sim 2.5$, was estimated on the basis of a titration experiment. More surplus of amine does not strongly effect changes in the absorption spectra. The dependence of the amount of triethylamine on changes of the absorption spectra upon lithium complexation is shown in Figure 3a.

Under such conditions, 'free' ligand and its lithium complex bands are separated by 46 nm and no interference from sodium and potassium cations is observed (Fig. 3b).

In compound **4**, the alkyl (*n*-hexyl) residue and the hydroxyl group are located at the same benzene residue. For comparison, when an alkyl substituent (e.g., *n*-pentadecyl) is present in the neighboring benzene ring, the complex absorption band is shifted only by about 20 nm.[19]

Based on ^{1}H NMR spectroscopic measurements it was established that in neutral acetonitrile, in the presence of 10-fold lithium perchlorate excess, the hydrazone and azo forms of compound **4** exist in a 3:1 ratio (1:1 for compound **1**[7]). In basic acetonitrile solution in the presence of lithium salt, only one tautomeric form, probably the ionized hydrazone, is present.

Analogous experiments were carried out for compound **5** with a nitro group in the *para* position to the azo group, localized in the neighboring benzene unit than the OH group (Scheme 1).

In pure acetonitrile, only in the presence lithium salt, small changes in absorption spectra were observed. Thus, metal cation complexation was studied in the presence of triethylamine. It was found that even a 1000-fold excess of triethylamine does not cause changes in ligand UV–vis spectrum, but addition of an organic base plays an important role in lithium complexation. Absorption spectra in the presence of a 500-fold excess of alkali metal perchlorates and different amounts of organic base were registered. The spectra in the presence of lithium and sodium salts are shown in Figure 4.

The most favorable changes, e.g., the least influence from sodium cation on selective lithium complexation, in UV–vis spectra were obtained upon a 4000-fold excess of amine addition (not shown here). In this case, separation of bands for free ligand and its lithium complex equals 95 nm and complexation is accompanied by a color change from yellow to violet-pink (Fig. 5).

Lithium cation complexation by **5** was also studied using ^{1}H NMR spectroscopy. Addition of an excess of lithium perchlorate in neutral acetonitrile causes only a small shift of the signals for the hydrazone form toward higher ppm values (the azophenol form was not observed in this case). Figure 6 shows the ^{1}H NMR spectra in the range of 3–13 ppm for **5** in *d*-acetonitrile, in the presence of triethylamine, and both in the presence of an organic base and lithium perchlorate. Addition of triethylamine causes no changes in the ^{1}H NMR spectrum, whereas in the presence of lithium perchlorate the signals of the aromatic protons are broadened (except for the proton in the *ortho* position to the nitro group, *para* to the alkoxy) and shifted downfield (especially the proton in the *ortho* position to the hexyl residue (7 ppm), for which position changes are probably connected with ionization of the molecule). Moreover, the signal of the OH proton at ~12.6 ppm disappears.

For 16-membered crown **6** in the same way as for compound **5**, only small changes in the absorption spectra were observed in the presence of alkali metal perchlorates in pure acetonitrile.

Thus, also in this case, metal cation interaction was studied in the presence of an organic base. The spectra of ligand **6** in the presence of different amounts of triethylamine were registered. The results are shown in Figure 7. Interestingly, for 16-membered

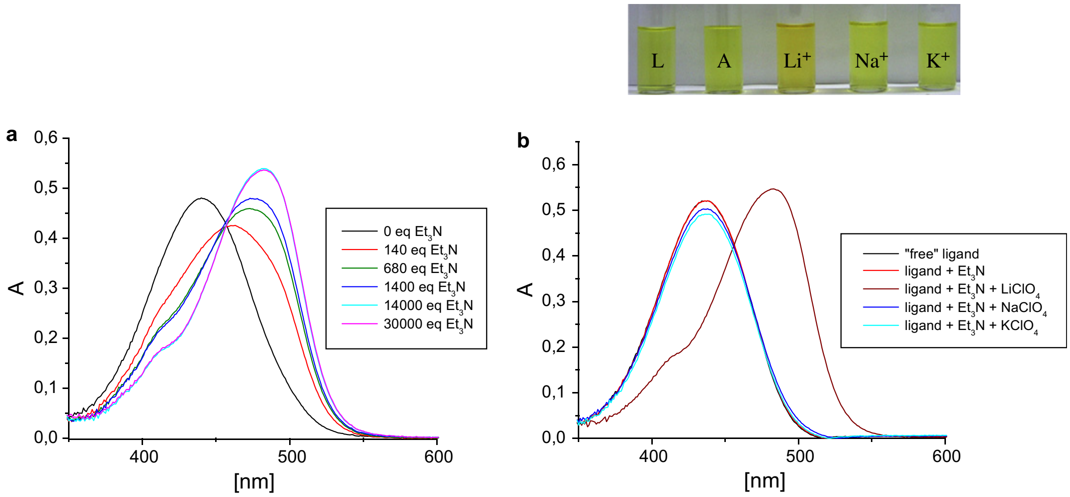


Figure 3. a) Dependence of amount of triethylamine on changes of absorption spectra of compound **4** (C_L=17.5 μM) upon lithium complexation (500-fold excess to crown; mol/mol); b) Changes in absorption spectra of compound **4** (C_L=17.5 μM) in the presence of alkali metal perchlorates: (500-fold excess to crown mol/mol) and triethylamine (A) (excess to crown ~14,000 mol/mol) in acetonitrile. Inset: color changes of ligand (L) **4** solution in the presence of triethylamine and metal perchlorates.

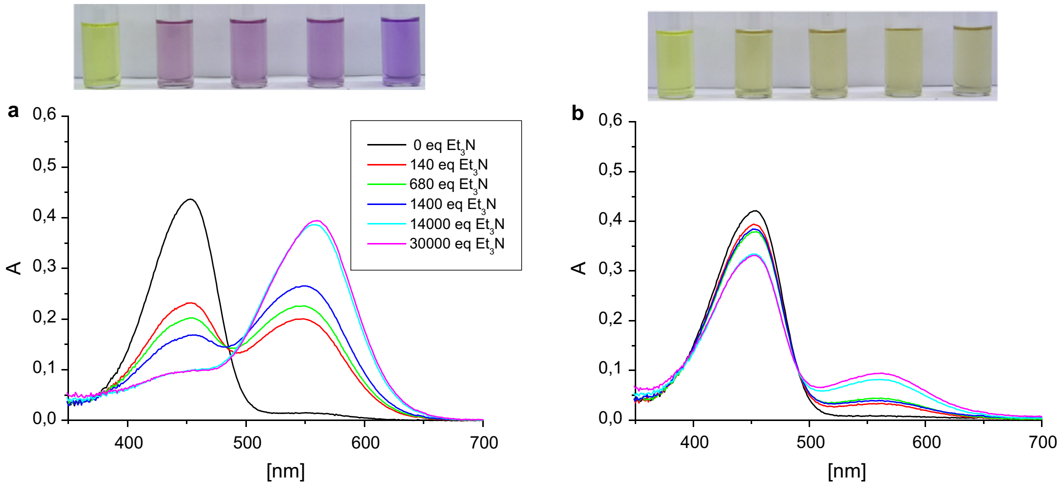


Figure 4. The dependence of triethylamine amount on changes of absorption spectra of compound **5** (C_L=17,5 µM) upon interaction with: a) lithium b) sodium in acetonitrile. 500-Fold salts excess to crown mol/mol. Solution colors correspond to (from left): 0, 140, 680, 1400 and 14,000 equiv of triethylamine.

crown **6**, the effect of addition of the organic base is the strongest compared to the smaller, 13-membered analogs. The presence of triethylamine probably causes proton abstraction from the hydrazone form, which is easier, in this case, due to a weaker hydrogen bond.

A series of experiments with different concentration of triethylamine showed that the optimal amount of organic base needed for selective response toward metal cations is 140 equiv (mol/mol to ligand). Changes in the absorption spectra in the presence of 500-fold excess of lithium, sodium or potassium salts without amine and in the presence of different amounts of triethylamine are shown in Figure 8.

The changes in absorption spectra and the accompanying changes of solution color for compound **6** in the presence of 500-fold excess of alkali metal perchlorates and 140 equiv of triethylamine are shown in Figure 9a. Under these conditions the difference in absorption maxima position between the ligand spectrum and the spectra registered in the presence of metal salts are 80, 106 and 112 nm for lithium, sodium, and potassium, respectively. This means that lithium, sodium, and potassium cations can be distinguished. An increase of the amine concentration and keeping a 500-fold excess of metal salts results in the formation of a blue–violet potassium complex (Fig. 9b).

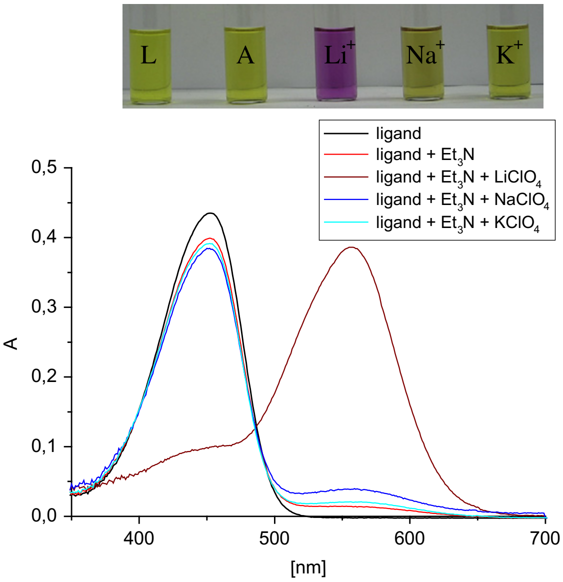


Figure 5. Changes in absorption spectra for compound **5** (C_L=17.5 µM) in the presence of 500-fold excess of alkali metal perchlorates and 4000 equiv of triethylamine (A) in acetonitrile. Inset: color changes of ligand **5** solution in the presence of triethylamine and metal perchlorates.

In the ^{1}H NMR spectrum of compound **6**, the NH proton was not observable after adding the amine. Signal of the proton at 7.0 ppm, in basic acetonitrile, is partly shifted to 7.4 ppm, which probably corresponds to the ionized form. The changes in the ^{1}H NMR spectra in the presence of lithium and sodium perchlorates and triethylamine in acetonitrile are shown in Figure 10. In the presence of these cations, the signal of the proton at 7.0 ppm disappears, and changes in positions of both the aromatic and ether signals are observed. Addition of a potassium salt, 30-fold excess, (spectrum not shown here) causes only a small increase of ionization degree, which is concluded from observation of the increasing integration of signal at 7.4 ppm.

The response for magnesium and calcium ions was also investigated under selected conditions. For 13-membered crowns **4** and **5**, the need for using a large excess of amine causes precipitation of a colored solid in the presence of magnesium and calcium perchlorates.

For the 16-membered crown **6**, where a smaller amount of organic base is used, significant changes in absorption spectra were observed in the presence of a calcium salt, whereas for magnesium, changes were negligible. The interaction with calcium ions is manifested by a color change from yellow to red ($\Delta\lambda$=74 nm) in the presence of 25 equiv of triethylamine. Precipitation of solid occurs upon higher concentration of amine (140 equiv) and is almost complete in the presence of about 1400 equiv of triethylamine. The changes in absorption spectra for compound **6** in the presence of magnesium and calcium are shown in Figure 11.

3. Conclusions

The steric hindrance caused by the *n*-hexyl residue in 5-*n*-hexyl-2,2′,4-trihydroxyazobenzene decreases the reactivity of the neighboring OH group in the alkylation reaction causing a higher efficiency of azobenzocrowns ether synthesis with peripheral hydroxyl group (compounds **4**–**6**) in the synthetic procedure. Using nitroderivative of hydroxyphenylazoresorcinol enables a simple synthesis of hydroxyazobenzocrowns with two peripheral groups, i.e., nitro and hydroxyl groups at two opposite sides of the conjugated chromophoric system.

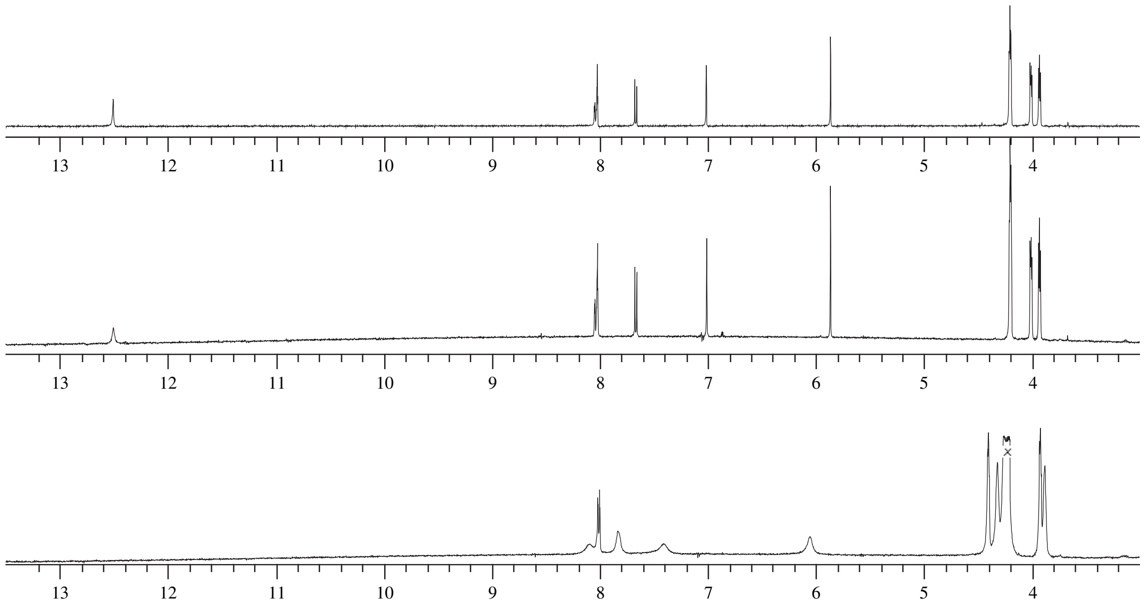


Figure 6. Plots of ^{1}H NMR spectra (*d*-acetonitrile) of: **5** (top); **5** in the presence of triethylamine (middle) and both in the presence triethylamine and lithium perchlorate (bottom).

The synthesized 13-membered macrocycles **4** and **5** selectively bind the lithium cation in the presence of sodium and potassium cations in basic (Et_3N) acetonitrile solution. The presence of magnesium and calcium salts does not affect selectivity. The hexyl residue increases the tendency of the mentioned compounds to exist in the hydrazone form. It also causes slightly larger bathochromic shift upon lithium cation complexation compared with analogous unsubstituted crown (compound **1**). The most significant color and spectral changes, in the visible range, in the presence of this cation were found for 13-membered hydroxyazobenzoazocrown with a nitro substituent in benzene ring (compound **5**); separation of bands in this case is 95 nm. It was demonstrated that changes upon lithium complexation are dependent on the kind of substituent in benzene ring(s) and their location. The 16-membered crown **6** interacts with more, among those investigated, metal cations: lithium, sodium and calcium. This means that the crown ether of the larger macrocycle is more sensitive, but less selective. The chromoionophoric behavior of the synthesized compounds potentially allows their application, under selected conditions, for construction of optical sensors.

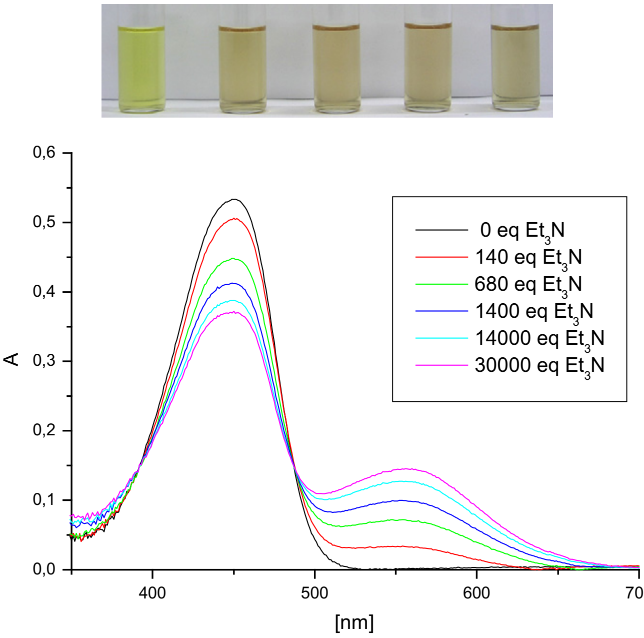


Figure 7. Changes in absorption spectra of compound **6** in acetonitrile (C_L=17,5 μM) in the presence of different amounts of triethylamine. Solution colors correspond to 0, 140, 680, 1400 and 14,000 equiv of triethylamine, respectively.

4. Experimental

4.1. General

All solvents were of analytical reagent grade. Tetrahydrofuran was distilled over $LiAlH_4$ and stored over molecular sieves. For spectrophotometric measurements HPLC grade solvents were used. The reagents from Aldrich (2-amino-5-nitrophenol and 4-hexylresorcinol) were used without further purification. Silica gel 60 (63–200 μm) (Merck) was used for column chromatography. TLC: aluminium sheets covered with $60F_{254}$ were from Merck, dichloromethane–acetone (10:1) was used as mobile phase. ^{1}H NMR spectra were recorded on Varian instrument at 500 MHz. Chemical shifts are reported as δ [ppm] values in relation to TMS. FTIR spectra were recorded on Mattson Genesis II instrument. UV–vis spectra were recorded on UNICAM UV 300 apparatus. Mass spectrometry was conducted on an AMD-604 apparatus (EI method, 70 eV) and Mariner (ESI method).

4.2. Synthesis

5-*n*-Hexyl-2,2′,4-trihydroxyazobenzene (**7**) and 5-*n*-hexyl-2,2′,4-trihydroxy-4′-nitro-azobenzene (**8**). A suspension of 2-aminophenol (1.76 g, ~16 mmol) or 2-amino-5-nitrophenol (90%, 2.46 g, ~16 mmol) in water (40 mL) was cooled and acidified with conc. hydrochloric acid (4 mL). The formed solution was diazotized with sodium nitrite (1.1 g in 8 mL cold water) and the reaction mixture was kept at 5 °C for 10 min. The obtained diazonium salt was added dropwise to an ice-cold solution of 4-hexylresorcinol (3.1 g, 16 mmol) and NaOH (2.0 g) in water (40 mL). The reaction mixture was stirred at 5 °C for 1 h. The mixture was acidified (HCl) and the precipitated solid was separated, washed with 0.1 M HCl and water, and dried in vacuum at room temperature. The crude compounds (quantitative yields) were used for synthesis of macrocycles. Mp 180–182 °C (**7**) and 175–176 °C (**8**).

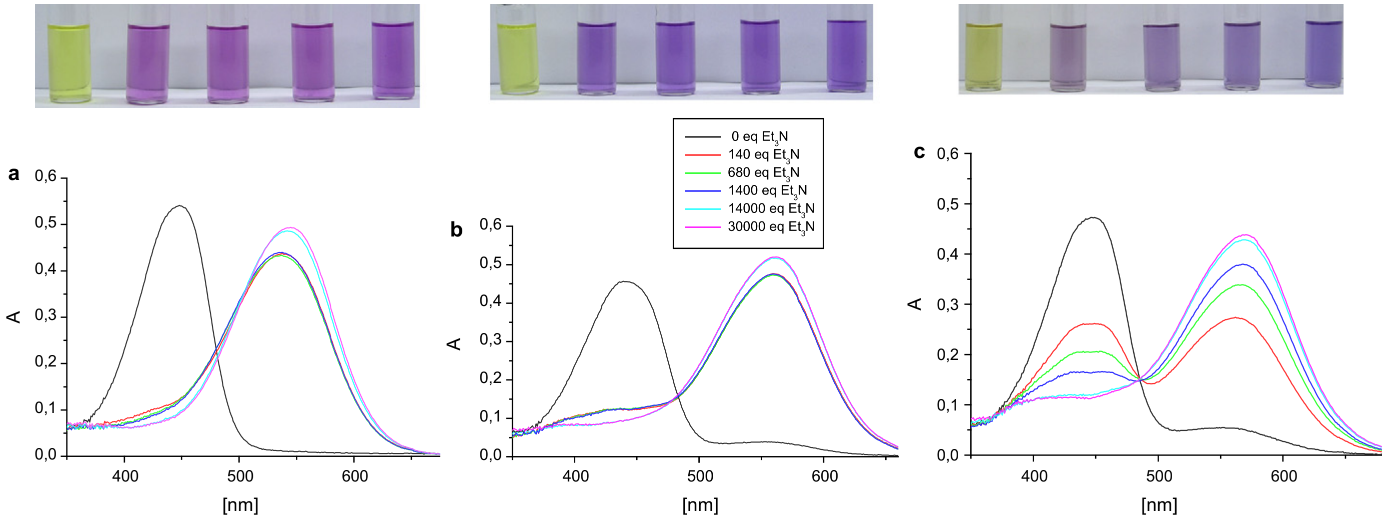


Figure 8. Changes in absorption spectra of compound **6** (C_L=17.5 μM) in the presence of 500-fold excess of: a) lithium, b) sodium and c) potassium perchlorates and different amounts of triethylamine in acetonitrile. Solution colors correspond to (from left): 0, 140, 680, 1400 and 14,000 equiv of triethylamine, respectively.

*4.2.1. Compound **7**.* ^{1}H NMR (d-DMSO): 0.86 (3H, t, J=6.6 Hz); 1.23–1.35 (6H, m); 1.48–1.57 (2H, m); 2.47 (2H, t, J=7.8 Hz); 6.34 (1H, s); 6.95 (1H, t, J=7.6 Hz); 6.99 (1H, d, J=7.3 Hz); 7.24 (1H, dt, J_1=7.6 Hz, J_2=1.5 Hz); 7.44 (1H, s); 7.72 (1H, dd, J_1=7.8 Hz, J_2=1.5 Hz); 11.4 (1H, br s); 12.7 (1H, br s). MS (EI) m/z: 314 (M^+).

*4.2.2. Compound **8**.* ^{1}H NMR (d-DMSO): 0.86 (3H, t, J=7.1 Hz); 1.22–1.35 (6H, m); 1.48–1.54 (2H, m); 2.43 (2H, t, J=7.6 Hz); 6.00 (1H, s); 7.17 (1H, s); 7.75 (1H, s); 7.79 (2H, s); 11.5 (1H, br s); 14.6 (1H, br s). MS (EI) m/z: 359 (M^+).

*4.2.3. Hydroxyazobenzocrown ethers **4**–**6**.* To 5-*n*-hexyl-2,2′,4-trihydroxyazobenzene (0.74 g, 2.33 mmol) or 5-*n*-hexyl-2,2′,4-trihydroxy-4′-nitro-azobenzene (0.85 g) potassium *tert*-butoxide (0.78 g, 7 mmol) in dry THF (50 mL) was added. The mixture was stirred for 0.5 h at room temperature and then 18-crown-6 (20 mg) was added. After that, the appropriate ditosyl derivative (2.2 mmol) in THF (50 mL) was added dropwise over 1 h. The reaction mixture was maintained at 70 °C for 24 h. The solid was removed by filtration and washed with THF until colorless filtrate was obtained. The filtrate was evaporated under reduced pressure, the residue was dissolved in methylene chloride and chromatographed on column using methylene chloride, methylene chloride/acetone mixtures and finally methylene chloride/acetone mixture (10:1) as eluents. The fractions containing the azobenzocrown ether were evaporated. Crystallization from acetone–hexane mixture gave compounds (dark orange solids): **4** (yield 12%, mp 120–121 °C, R_f=0.22), **5** (yield 10%, mp 190–191 °C, R_f=0.44) or **6** (yield 7%, mp 195–196 °C, R_f=0.33), respectively.

*4.2.4. Compound **4**.* ^{1}H NMR (d-acetone): 0.91 (3H, t, J=6.8 Hz); 1.28–1.42 (6H, m); 1.54 (2H, q, J=7.4 Hz); 2.41 (2H, t, J=7.4 Hz); 3.97 (2H, t, J=4.3 Hz); 4.10–4.12 (2H, m); 4.18 (2H, t, J=4.3 Hz); 4.29–4.31 (2H, m); 5.87 (1H, s); 7.03 (1H, s); 7.06 (1H, dt, J_1=7.6 Hz, J_2=1.3 Hz); 7.16 (1H, t, J=7.2 Hz); 7.25 (1H, dd, J_1=7.6 Hz, J_2=1.2 Hz); 7.64 (1H, dd, J_1=7.8 Hz, J_2=1.3 Hz); 12.48 (1H, s). IR (Nujol) cm^{-1}: 3277, 1636, 1599, 1570, 1523, 1261, 1238, 1189, 1128, 1090, 722 cm^{-1}. UV–vis (acetonitrile): λ_{max}=435 nm, ϵ_{max}=2.52×10^4. HRMS (EI) m/z: 384.2041 (calcd for $C_{22}H_{28}N_2O_4$ 384.2049).

*4.2.5. Compound **5**.* ^{1}H NMR (d-acetone): 0.89–0.93 (3H, m); 1.30–1.42 (6H, m); 1,51–1.58 (2H, m); 2.42 (2H, t, J=7.6 Hz); 4.04 (2H, t,

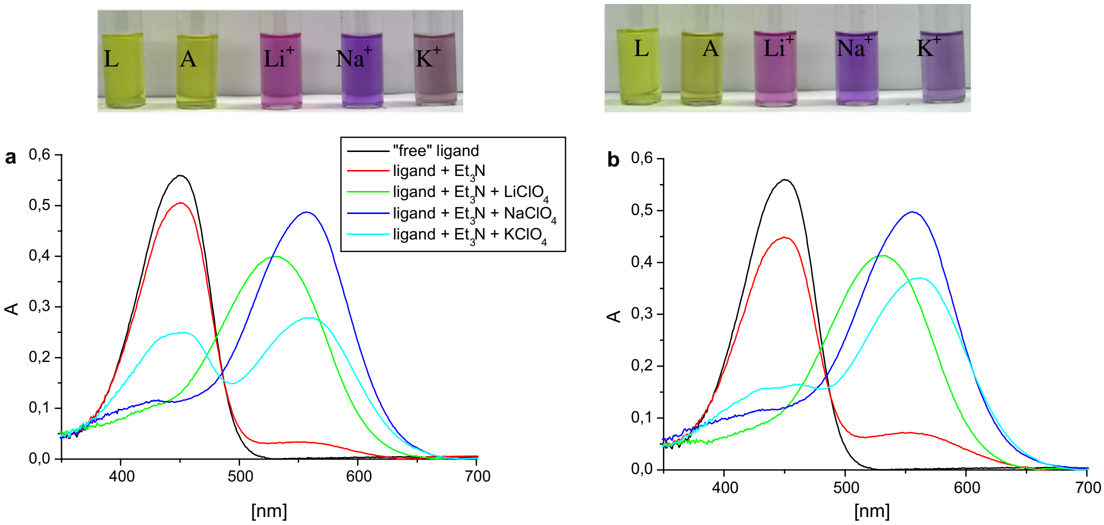


Figure 9. Changes in absorption spectra for compound **6** in the presence of 500-fold excess of alkali metal perchlorates and a) 140 equiv and b) 1400 equiv of triethylamine in acetonitrile. Inset: color changes of ligand **6** solution in the presence of triethylamine and metal perchlorates.

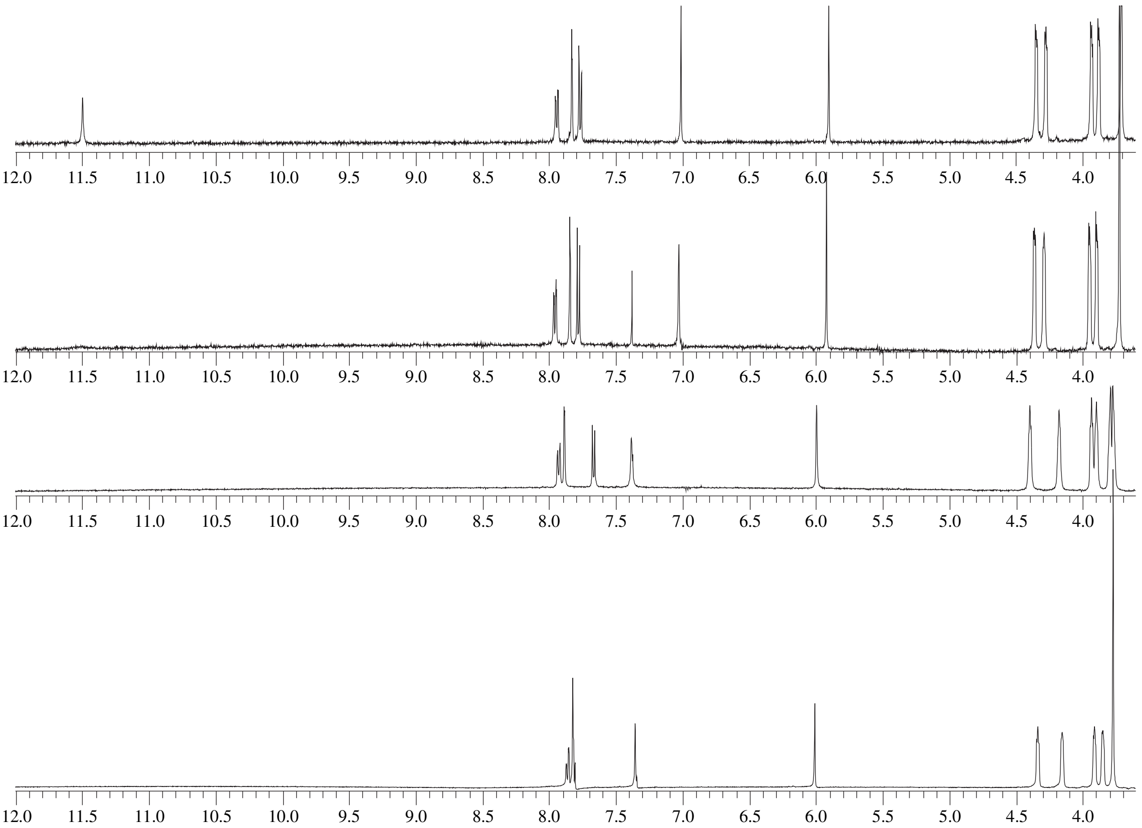


Figure 10. Plots of ^{1}H NMR spectra *d*-acetonitrile) (from the top) of: **6**; **6** in the presence of triethylamine, both in the presence of triethylamine and lithium perchlorate and both in the presence triethylamine and sodium perchlorate.

J=4.2 Hz); 4.12–4.16 (2H, m); 4.33–4.40 (4H, m); 5.94 (1H, s); 7.05 (1H, s); 7.75 (1H, d, *J*=9.8 Hz); 8.06–8.11 (2H, m); 12.56 (1H, s). IR (Nujol) cm^{-1}: 3255, 1637, 1592, 1575, 1528, 1508, 1321, 1283, 1254, 1238, 1189, 1167, 1132, 1079, 937, 724 cm^{-1}. UV–vis (acetonitrile): λ_{max}=451 nm, ϵ_{max}=3.20×10^4. HRMS (EI) *m*/*z*: 429.1906 (calcd for $C_{22}H_{27}N_3O_6$ 429.1900).

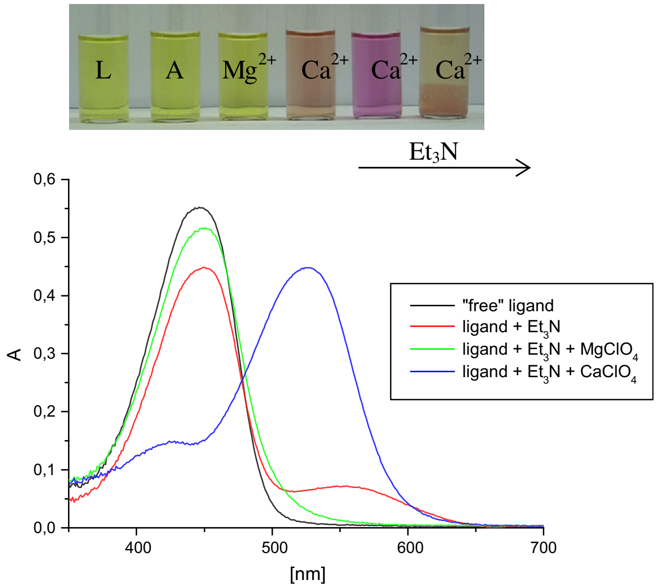


Figure 11. Changes in absorption spectra for compound **6** (C_L=17.5 μM) in the presence of 500-fold excess of magnesium or calcium perchlorates and 140 equiv or 25 equiv of triethylamine, respectively, in acetonitrile. Inset: color changes of ligand **6** solution in the presence of triethylamine and metal perchlorates. For calcium additionally in the presence of 140 and 1400 equiv of triethylamine.

*4.2.6. Compound **6**.* ^{1}H NMR (d-acetone): 0.87–0.94 (3H, m); 1.28–1.42 (6H, m); 1,50–1.58 (2H, m); 2.42 (2H, d, *J*=7.0 Hz); 3.80 (4H, s); 4.02 (2H, s); 4.09 (2H, s); 4.43 (2H, s); 4.53 (2H, s); 5.99 (1H, s); 7.07 (1H, s); 7.86 (1H, d, *J*=8.7 Hz); 7.92 (1H, s); 8.00 (1H, d, *J*=8.7 Hz); 11.61 (1H, s). IR (Nujol) cm^{-1}: 3300, 1636, 1591, 1573, 1524, 1502, 1335, 1271, 1236, 1217, 1168, 1124, 1093, 1040, 950, 900, 880, 720. UV–vis (acetonitrile): λ_{max}=451 nm, ϵ_{max}=3.65×10^4. HRMS (ESI) *m*/*z*: 496.2047 [M+Na]$^+$ (calcd for $C_{24}H_{31}N_3O_7Na$ 496.2054).

4.3. UV–vis studies

The stock solutions of azobenzocrowns (10^{-4} M) and metal perchlorates (10^{-2} M) were prepared by weighing the respective quantities of them and dissolving in 10 mL volumetric flasks in acetonitrile. Series of working solutions of constant concentration of ligand, to which triethylamine and salt solutions were added in demanded amounts keeping total volume constant (3 mL). Spectra of such prepared solutions were registered.

The stability constant of complex of compound **4** with lithium cation was calculated with the use of OPIUM[20] program on the basis of titration experiment data.

Acknowledgements

The authors kindly acknowledged support from sources for science in years 2008–2010, Grant Nr. N N204 223834. The authors also thank Prof. J.F. Biernat for manuscript valuable discussions and Mrs. J. Żochowska for technical assistance.

References and notes

1. For example see review: Luboch, E.; Bilewicz, R.; Kowalczyk, M.; Wagner-Wysiecka, E.; Biernat, J. F. *Azo Macrocyclic Compounds, in Advances in Supramolecular Chemistry*; Gokel, G., Ed.; Cerberus: South Miami, USA, 2003; Vol. 9, p 71.
2. (a) Shiga, M.; Takagi, M.; Ueno, K. *Chem. Lett.* **1980**, 1021; (b) Shiga, M.; Nakamura, H.; Takagi, M.; Ueno, K. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 412; (c) Tahara, R.; Morozumi, T.; Nakamura, H.; Shimomura, M. *J. Phys. Chem. B* **1997**, *101*, 7736.
3. (a) Biernat, J. F.; Luboch, E.; Cygan, A.; Simonov, Yu. A.; Dvorkin, A. A.; Muszalska, E.; Bilewicz, R. *Tetrahedron* **1992**, *48*, 4399; (b) Luboch, E.; Biernat, J. F.; Muszalska, E.; Bilewicz, R. *Supramol. Chem.* **1995**, *5*, 201; (c) Luboch, E.; Biernat, J. F.; Simonov, Yu. A.; Dvorkin, A. A. *Tetrahedron* **1998**, *54*, 4977; (d) Pijanowska, D. G.; Luboch, E.; Biernat, J. F.; Dawgul, M.; Torbicz, W. *Sens. Actuators B* **1999**, *58*, 384; (e) Zawisza, I.; Bilewicz, R.; Luboch, E.; Biernat, J. F. *Thin Solid Films* **1999**, *348*, 173.
4. (a) Saadioui, M.; Reynier, N.; Dozol, J. F.; Asfari, Z.; Vicens, J. *J. Inclusion Phenom. Mol. Recognit. Chem.* **1997**, *29*, 153; (b) Pipoosananakaton, B.; Sukwattanasinitt, M.; Jaiboon, N.; Chaichit, N.; Tuntulani, T. *Tetrahedron Lett.* **2000**, *41*, 9095.
5. (a) Shinkai, S. *Switchable Guest-Binding Receptor Molecules in Comprehensive Supramolecular Chemistry*; Gokel, G. W., Ed.; Pergamon: New York, NY, 1996; Vol. 1, p 671; (b) Hayashita, T.; Takagi, M. *Chromoionophores Based on Crown Ethers and Related Structures in Comprehensive Supramolecular Chemistry*; Gokel, G. W., Ed.; Pergamon: New York, NY, 1996; Vol. 1, p 635; (c) McKervey, M.A.; Schwing-Weyl, M.-J.; Arnaud-Neu, F. *Cation Binding by Calixarenes in Comprehensive Supramolecular Chemistry*; Gokel, G. W., Ed.; Pergamon: New York, NY, 1996; Vol. 1, p 537; (d) Shinkai, S.; Manabe, O. *Top. Curr. Chem.* **1984**, *121*, 67; (e) Shinkai, S.; Takeuchi, M.; Ikeda, A. In *Polym. Sens. Actuators*; Osada, Y., De Rossi, D. E., Eds.; Springer: Berlin, Germany, 2000; pp 183–206.
6. (a) Chapoteau, E.; Czech, B. P.; Gebauer, C. R.; Kumar, A.; Leong, K.; Mytych, D. T.; Zazulak, W.; Desai, D. H.; Luboch, E.; Krzykawski, J.; Bartsch, R. A. *J. Org. Chem.* **1991**, *56*, 2575; (b) Misumi, S. *Mem. Inst. Sci. Ind. Res. Osaka Univ.* **1991**, *48*, 9; (c) Czech, B. P.; Kumar, A.; Chapoteou, E. *Lithium* **1994**, *5*, 11; (d) Misumi, S. *Top. Curr. Chem.* **1993**, *165*, 163; (e) Kaneda, T. *Stud. Org. Chem. (Amsterdam)* **1992**, *45*, 311; (f) Misumi, S. *Kagaku to Kogyo (Tokyo)* **1993**, *46*, 756 C.A. 1993, 119, 45202j; (g) Naemura, K.; Takeuchi, S.; Asada, M.; Hirose, K.; Tobe, Y.; Kaneda, T.; Sakata, Y. *J. Chem. Soc., Chem. Commun.* **1994**, 711; (h) Naemura, K.; Takeuchi, S.; Asada, M.; Ueno, K.; Hirose, K.; Tobe, Y.; Kaneda, T.; Sakata, Y. *J. Chem. Soc., Perkin Trans. 1* **1995**, 1429; (i) Naemura, K.; Takeuchi, S.; Hirose, K.; Tobe, Y.; Kaneda, T.; Sakata, Y. *J. Chem. Soc., Perkin Trans. I* **1995**, 213; (j) Naemura, K.; Wakebe, T.; Hirose, K.; Tobe, Y. *Tetrahedron: Asymmetry* **1997**, *8*, 2585; (k) Ogasahara, K.; Hirose, K.; Tobe, Y.; Naemura, K. *J. Chem. Soc., Perkin Trans. 1* **1997**, 3227; (l) Naemura, K.; Matsunaga, K.; Fuji, J.; Ogasahara, K.; Nishikawa, Y.; Hirose, K.; Tobe, Y. *Anal. Sci.* **1998**, *14*, 175; (m) Naemura, K.; Nishioka, K.; Ogasahara, K.; Nishikawa, Y.; Hirose, K.; Tobe, Y. *Tetrahedron: Asymmetry* **1998**, *9*, 563; (n) Hirose, K.; Ogasahara, K.; Nishioka, K.; Tobe, Y.; Naemura, K. *J. Chem. Soc., Perkin Trans. 2* **1984**, 2000; (o) Hirose, K. *J. Incl. Phenom. Macrocycl. Chem.* **2001**, *39*, 193.
7. Luboch, E.; Wagner-Wysiecka, E.; Biernat, J. F. *J. Supramol. Chem.* **2002**, *2*, 279.
8. Luboch, E.; Wagner-Wysiecka, E.; Poleska-Muchlado, Z.; Kravtsov, V. Ch. *Tetrahedron* **2005**, *61*, 10738.
9. Luboch, E. *Pol. J. Chem.* **2008**, *82*, 1315.
10. (a) Wagner-Wysiecka, E.; Skwierawska, A.; Kravtsov, V. Ch.; Biernat, J. F. *J. Supramol. Chem.* **2001**, *1*, 77; (b) Inerowicz, H. D. *J. Inclusion Phenom.* **2001**, *39*, 211.
11. Wagner-Wysiecka, E.; Luboch, E.; Marczak, B.; Biernat, J. F. *Pol. J. Chem.* **2001**, *79*, 1457.
12. Cram, D. J.; Carmack, R. A.; Helgeson, R. C. *J. Am. Chem. Soc.* **1988**, *110*, 571.
13. Hofer, E.; Uffman, H. *Tetrahedron Lett.* **1971**, *35*, 3241.
14. Habibi, M. H.; Hassanzadeh, A.; Zeini-Isfahani, A. *Dyes & Pigments* **2006**, *69*, 93.
15. Dakiky, M.; Kanan, K.; Khamis, M. *Dyes & Pigments* **1999**, *41*, 199.
16. Antonov, L.; Kawauchi, S.; Satoh, M.; Komiyama, J. *Dyes & Pigments* **1999**, *40*, 163.
17. Kishimoto, S.; Kitahara, S.; Manabe, O.; Hiyama, H. *J. Org. Chem.* **1978**, *43*, 3882.
18. Luboch, E.; Kravtsov, V. Ch. *J. Mol. Struct.* **2004**, *699*, 9.
19. Luboch, E.; Wagner-Wysiecka, E. unpublished results.
20. Kyvala, M.; Lukeš, I.: Program Package "OPIUM" Available (free of charge) on http://www.natur.cuni.cz/∼kyvala/opium.html.