Spacer-Chromoionophores – Polymethine Dye Substituted Aza-Crown Ethers with Increased Complexation Ability

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Received August 5th, 1998, respectively November 11th, 1998

Keywords: Chromophores, Crown compounds, Dyes, Polymethines, Complexation Constants

Abstract. Aromatic aldehyde derivatives of *N*-phenyl-aza-15-crown-5 **2**, *N*-phenyl-aza-18-crown-6 **8**, and benzo-15-crown-5 **10** are condensed with malononitrile and 2-amino-1,1,3-tricyano-1-propene to give light yellow to orange colored crown ether derivatives **4**, **5a**, **9a**, **11**, and **12**. **5a** and **9a** were acylated with ethyl chloroformate to give the magenta colored dyes **5b** and **9b**, respectively. By condensation of *N*-(4-nitrosophenyl)-aza-15-crown-5 **3** with 2-amino-1,1,3-tricyano-1-propene the magenta dye **6a** is obtained. Acylation of **6a** with ethyl chloroformiate leads to the deep blue colored dye **6b**. In these derivatives the nitrogen or oxygen atoms of the crown ethers are part of the chro-mophoric system and binding properties are affected. Further chromophoric derivatives of aza-crown ethers are stu-died in which these are separated from the chromophoric moiety by a spacer. *N*-(*ω*-chloroalkyl)-*N*-alkylanilines **14a**–**c** were attached to aza-15-crown-5 **13a** and aza-18-crown-6 **13b** to yield the spacer crown ether derivatives **15a**–**c** and **16a**–**c**, respectively. The formylated spacer crown ether derivatives **17a**–**c** and **18b** were condensed with 2-amino-1,1,3-tricyano-1-propene to give the orange spacer-chromoionophores **19a**–**c** and **20**. In these crown ether derivatives the extended conjugation is interrupted by the spacer and good binding properties are obtained. The complex formation constants of the crown ether derivatives with Na^+ and K^+ are determined using ^1H NMR spectroscopy.

Chromoionophores are crown ether derivatives, which contain a chromophoric group [1–3]. These functional dyes are of a great interest for analytical applications [4, 5], especially in medical diagnostics and therapy. A great number of chromo- and also fluoroionophores, starting from aldehydes of *N*-phenyl-aza-15-crown-5 or *N*-phenyl-aza-18-crown-6 are described in the literature [6–11]. Substitution of the aminic H-atom in aza-crowns leads to nitrogen-pivot lariat crowns, and it was shown that alkyl groups increase the binding strength of the metal complexes [12–14]. The present paper deals with the synthesis of deeply colored polymethine crown ether derivatives and the influence of the electron acceptor properties of the side chain on the complexation, depending upon conjugation of the chromophore with the nitrogen of the aza-crowns.

Synthesis of the Chromoionophores 4, 5, 6, 9, 11, and 12 Starting from *N*-Phenyl-aza-15-crown-5, *N*-Phenyl-aza-18-crown-6, and Benzo-15-crown-5

4-(1,4,7,10-Tetraoxa-13-aza-13-cyclopentadecyl) benzaldehyde **2** was synthesized by Vilsmeier formylation of *N*-phenyl-aza-15-crown-5 **1** with phosphorus oxytrichloride and *N*,*N*-dimethylformamide according to the procedure described by Dix and Vögtle [6]. Reaction of the crown ether aldehyde **2** with malononitrile and dimeric malononitrile (2-amino-1,1,3-tricyanopropene), respectively, is a Knoevenagel condensation which occurs under mild conditions using piperidine as catalyst. The yellow colored chromoionophores **4** and **5a**, showing UV/Vis absorption maxima at about λ_{max} = 430 nm, are obtained with a quite good yield.

13-(4-Nitrosophenyl)-1,4,7,10-tetraoxa-13-azacyclopentadecane **3** was as well prepared according to Dix and Vögtle [6]. With the dimeric malononitrile it afforded with good yield the magenta colored dye **6a** (λ_{max} = 524 nm, CH_3CN).

N-Phenyl-aza-18-crown-6 **7** was synthesized according to Dix und Vögtle [6], and the corresponding aldehyde **8** similarly to the crown ether aldehyde **2** prepared by Vilsmeier formylation. Formation of side products is appreciable, the aldehyde can be purified by column chromatography. Condensation of the crown ether aldehyde **8** with dimeric malononitrile and piperidine acetate as catalyst at 55 °C yielded the yellow chromoionophore **9a** showing an UV/Vis absorption maximum at λ_{max} = 426 nm.

The *N*,*N*-bis-acylation of the primary amino group in the condensation products **5a**, **6a**, and **9a** is a known method to obtain a strong bathochromic shift in UV/Vis spectra of polymethine cyanines which contain the dimeric malononitrile as polymethine backbone [15]. After workup of the reaction mixtures, the acylated dyes **5b**, **6b**, and **9b** are obtained in very good yields as crys-

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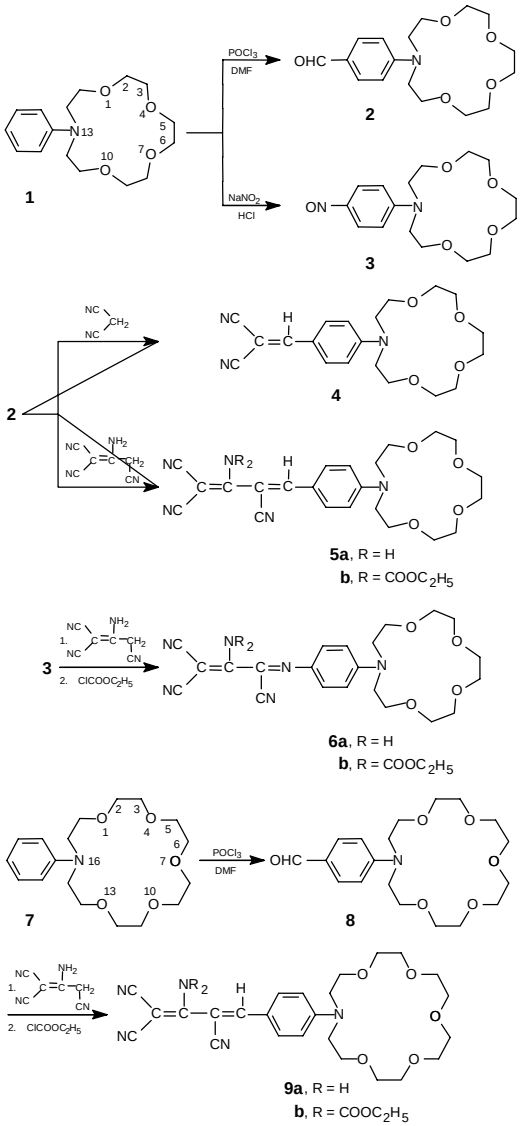
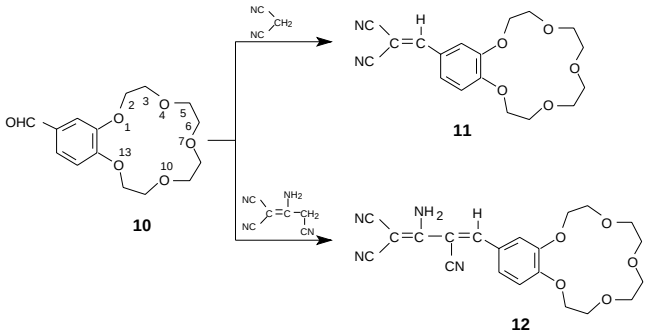


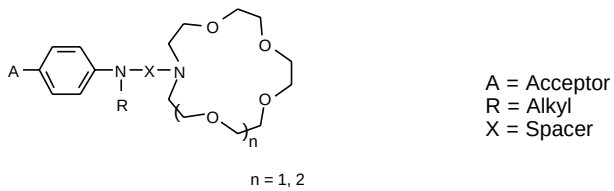
talline compounds showing UV/Vis absorption maxima at λ_{max} = 539, 614, and 541 nm, respectively.

4'-Formylbenzo-15-crown-5 **10** was synthesized from benzo-15-crown-5 by Vilsmeier formylation according to the method described by Hyde *et al*. [16] or by introduction of the carbonyl group with hexamethylenetetramine and trifluoroacetic acid according to Wada *et al*. [17]. For the condensation with malononitrile or 2-amino-1,1,3-tricyanopropene cadmium iodide must be used as catalyst, according to Prajapati and Sandhu [18]. The chromophoric derivatives **11** and **12** are significantly lighter colored than the corresponding condensation products **4**, **5a**, and **9a** of the aza-crown aldehydes **2** and **8**. Substitution of the crown ether nitrogen atom by oxygen causes a hypsochromic shift of $\Delta\lambda$ = 60–70 nm due to the weaker donor effect of oxygen compared to nitrogen (λ_{max} = 370 and 360 nm, respectively).



Synthesis of *N*-(*N*-Alkyl-*N*-phenylamino-alkyl)-aza-15-crown-5 and -aza-18-crown-6 Derivatives 17, 18, 19, and 20 (Spacer-Chromoionophores)

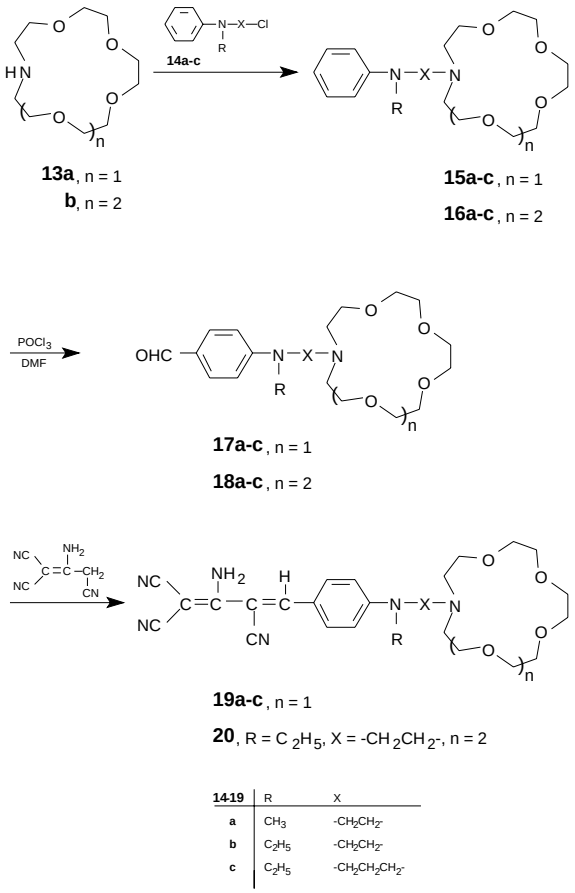
The synthesized crown ethers with chromophoric groups **4**, **5a**–**b**, **6a**–**b**, **9a**–**b**, **11**, and **12** provide as expected only weak binding constants. This can be explained, naturally apart from the influence of the crown cavity size, by the strong electron withdrawing effect of the dicyanomethylene group which is directly conjugated with the aza-crown nitrogen atom or the benzo-15-crown-5 oxygen, respectively. Therefore, it should be tried to separate the chromophoric moiety of such compounds from the crown by a suitable spacer. Thus, the conjugation with the crown nitrogen is interrupted whereby, at similar UV/Vis absorption maxima of the products, good complexation properties should be given (Scheme 1).



Scheme 1 Spacer-Chromoionophores

A synthetic concept was developed to convert *N*-alkylanilines into *N*-hydroxyalkyl-*N*-alkylanilines [19] which were then transformed into the corresponding chloro derivatives **14a**–**c** [20]. These were attached to the aza-crowns **13a**–**b** to give the crown ether derivatives **15a**–**c** and **16a**–**c** which formylated to **17a**–**c** and **18a**–**c** finally yielded with dimeric malononitrile the desired products **19a**–**c** and **20** called by us spacerchromoionophores.

The spacer-chromoionophores fulfill regarding their color properties our expectations, they show as compared to the homologous chromoionophores **5a** and **9a** even a small bathochromic shift (λ_{max} between 444 and 452 nm). The complexation constants exhibit values



14-19	R	X
a	CH_3	$-CH_2CH_2-$
b	C_2H_5	$-CH_2CH_2-$
c	C_2H_5	$-CH_2CH_2CH_2-$

showing a large increase as compared to the chromoionophores described before (see Complexation Constants and Discussion).

Complexation Constants

The complexation constants were determined by ^{1}H NMR spectroscopy according to Geringer and Sterk [21] by measuring the chemical shifts of the crown ether H-atoms of the free form and in the presence of different concentrations of alkali metal cations. Usually for crown ethers a fast exchange between ligand and ion occurs and only a single signal can be detected. The measured chemical shift corresponds to an averaged value between the free and the complexed form of the ligand. The variation of the chemical shift is described by following equation:

$$\delta_m = (C_{L\ free} \cdot \delta_{L\ free} + C_C \cdot \delta_C) \cdot C_{L\ tot}^{-1} \quad (1)$$

δ_m = measured (average) chemical shift
δ_C = chemical shift of the complex
$\delta_{L\ free}$ = chemical shift of the free ligand
$C_{L\ free}$ = concentration of the free ligand
C_C = concentration of the complex
$C_{L\ tot}$ = total concentration of the ligand

The concentrations of the free and complexed species can be calculated from the well known complexation equilibrium:

$$K_c = C_C \cdot (C_{L\ free} \cdot C_{I\ free})^{-1} \quad (2)$$

K_c = complex formation constant
$C_{I\ free}$ = concentration of the free ions

Since the total concentrations of the ligand and ion are known and the chemical shift of the free ligand can be measured, K_c and δ_C are the unknown parameters determining the curve. The values for the unknown parameters are iteratively varied, and the deviations between the calculated and the measured values are minimized using a nonlinear least-squares fit procedure.

As salts sodium- and potassium thiocyanate were utilized. In Table 1, complex formation constants of the 1:1 complexes of the ligands with Na^+ and/or K^+ in [D_6]acetone are presented. The chromoionophore **9a** starting from the crown ether aldehyde **8** only shows, as already mentioned, in [D_6]acetone with Na^+ a binding constant K_c = 310, and with K^+ K_c = 50. The acylated dye **9b** provides with Na^+ in [D_4]methanol a complexation constant K_c = 24, and in [D_6]acetone K_c = 160, respectively. The benzo-15-crown-5 derivatives **11** and **12** show higher complexation constants than the corresponding *N*-phenyl-aza-18-crown-6 derivatives. For the condensation product with malononitrile **11** complex stability constants in acetone with Na^+ K_c = 3400, and with K^+ K_c = 3700 are obtained. The condensation product **12** with the dimeric malononitrile provides with Na^+

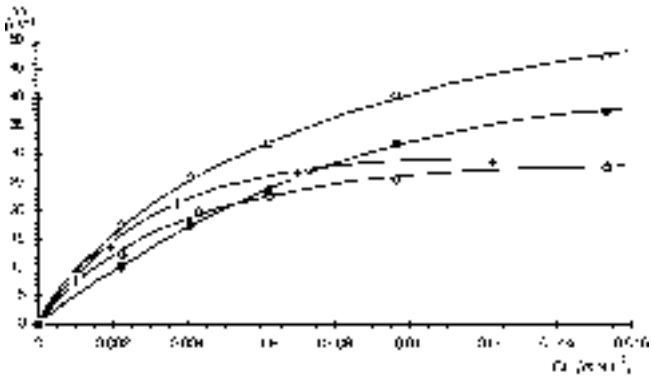


Fig. 1 Measured (o) and calculated (–) chemical shifts ($\Delta\delta$) of the H-atoms at C-15 and C-17 in **9a**, ($\Delta\delta_{complex}$ = 60, K_c = 310), measured (•) and calculated (–) chemical shifts ($\Delta\delta$) of the H-atoms at C-15 and C-17 in **9b**, ($\Delta\delta_{complex}$ = 58, K_c = 160), measured (◇) and calculated (–) chemical shifts ($\Delta\delta$) of the H-atoms at C-5, C-6, C-8, and C-9 in **11**, ($\Delta\delta_{complex}$ = 29, K_c = 3400), and measured (+) and calculated (–) chemical shifts ($\Delta\delta$) of the H-atoms at C-5, C-6, C-8, and C-9 in **12**, ($\Delta\delta_{complex}$ = 34, K_c = 610), plotted *vs*. the molar concentration of the sodium ions (CI) in acetone, related to the chemical shift of the free ligand

in acetone a complexation constant K_c = 610 (Table 1).

Fig. 1 shows the complex formation of **11** and **12**, with a curve reaching a plateau at relatively low ion concentrations, whereas for **9a** and **9b** the curve has a quite constant slope even at higher ion concentrations.

Chromoionophore **19a**, obtained by condensation of crown ether aldehyde **17a** with dimeric malononitrile, provides with Na^+ a complexation constant K_c = 12000, and with K^+ K_c = 1200, respectively. For the condensation product **19c** of aldehyde **17c** with the dimeric malononitrile constants K_c = 17000 with Na^+, and K_c = 1200 with K^+ are obtained. Dye **20**, starting from the spacer-crown ether aldehyde **18b**, provides with Na^+ a binding constant K_c = 28000, and with K^+ K_c = 62000, respectively (Table 1).

Fig. 2 shows the complex formation of **19a**, **19c**, and **20** with sodium ions, three compounds having very good complexation abilities, their curves reaching fast a plateau.

Fig. 3 shows the complex formation of **19a**, **19c**, and **20** with potassium ions, chromoionophores **19a** and **19c** forming with potassium, due to the too small crown cavity, weaker complexes than **20** where the plateau is reached only at higher ion concentrations.

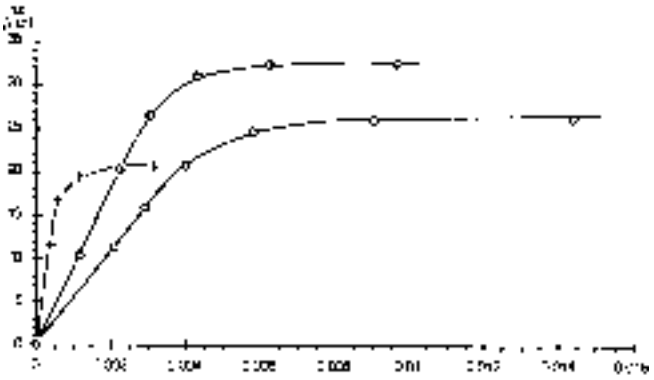


Fig. 2 Measured (o) and calculated (–) chemical shifts ($\Delta\delta$) of the H-atoms at C-5 and C-6 in **19a**, ($\Delta\delta_{complex}$ = 26, K_c = 12000), measured (+) and calculated (–) chemical shifts ($\Delta\delta$) of the H-atoms at C-5 and C-6 in **19c**, ($\Delta\delta_{complex}$ = 21, K_c = 17000), and measured ($\diamond$) and calculated (–) chemical shifts ($\Delta\delta$) of the H-atoms at C-5, C-6, C-8, and C-9 in **20**, ($\Delta\delta_{complex}$ = 35, K_c = 28000), plotted vs. the molar concentration of the sodium ions (CI) in acetone, related to the chemical shift of the free ligand

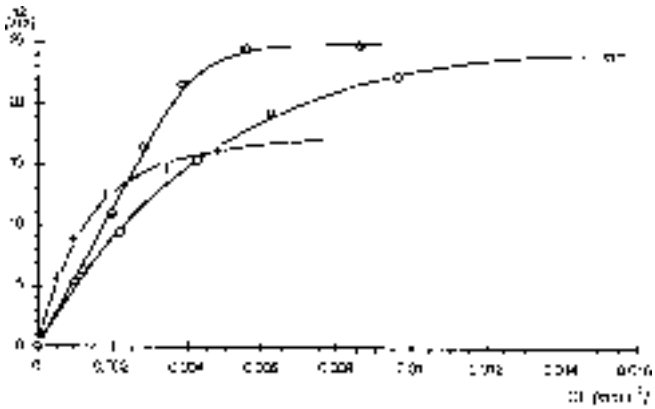


Fig. 3 Measured (o) and calculated (–) chemical shifts ($\Delta\delta$) of the H-atoms at C-5 and C-6 in **19a**, ($\Delta\delta_{complex}$ = 26, K_c = 1200), measured (+) and calculated (–) chemical shifts ($\Delta\delta$) of the H-atoms at C-5 and C-6 in **19c**, ($\Delta\delta_{complex}$ = 19, K_c = 1200), and measured ($\diamond$) and calculated (–) chemical shifts ($\Delta\delta$) of the H-atoms at C-5, C-6, C-8, and C-9 in **20**, ($\Delta\delta_{complex}$ = 25, K_c = 62000), plotted *vs*. the molar concentration of the potassium ions (CI) in acetone, related to the chemical shift of the free ligand

Discussion

The complex formation of various crown ethers and the influence of different substituents on the stability of the complexes was studied in many papers [22, 23]. However, a comparison of the stability constants is quite difficult because of the different determination methods employed. Besides, the utilized solvent is very important, too [24].

Thus, aza-15-crown-5 shows with Na^+ in methanol a binding constant K_c = 115 [25]. Substitution of the amine hydrogen atom by the phenyl-group in **1** decreases the complexation ability because of its acceptor effect (K_c = 6.82 – 7.90 [21]). The chromophoric derivatives **4**, **5a**–**b**, and **6a**–**b** of *N*-phenyl-aza-15-crown-5 **1** provide with Na^+ and K^+ only very small complexation constants. In these condensation products, the electron withdrawing effect of the chromophoric groups is very strong, and the crown-nitrogen atom is involved in the conjugation, which means that the nitrogen atom can only have a negligible role in the complexation.

Aza-18-crown-6 shows some selectivity for potassium. Okahara *et al*. [25] found for the complexation of aza-18-crown-6 with Na^+ K_c = 589, and with K^+ K_c = 15135, respectively. Also in case of *N*-phenyl-aza-18-crown-6 **7** the phenyl ring has a negative influence on the complexation ability because of its electron withdrawing effect. This effect is increased by further substitution with strong acceptor groups in the phenyl ring [26–28]. Chromophoric derivatives **9a**–**b** of *N*-phenyl-aza-18-crown-6 **7** provide higher complexation constants than the respective derivatives **5a**–**b** of *N*-phenyl-aza-15-crown-5 **1**, and the higher stability of the complexes is only due to the higher number of oxygen atoms in the crown. The expected selectivity for K^+ does not appear any more, because the stability constant of the complex with sodium (K_c = 310) is higher compared to the one with potassium (K_c = 50).

Complex formation is influenced also by the solvent used. In acetone, a 7-fold increase of the binding constant of chromoionophore **9b** as compared to methanol

is found (K_c = 160 and K_c = 24, respectively).

In the condensation products **11** and **12** of 4'-formylbenzo-15-crown-5 (**10**), the aromatic crown ether-oxygen atoms are less involved in the conjugation with the chromophoric part of the molecule and provide with respect to that much higher complexation constants than the comparable derivatives **4**, **5a**, and **9a** of the *N*-phenyl-aza-crowns **1** and **7**. **11** provides with Na^+ and K^+ complexes of comparable stability to those known from literature [29] for the unsubstituted benzo-15-crown-5. Because of the stronger acceptor effect of the chromophoric moiety in the condensation product **12** with dimeric malononitrile, the complex formation constant decreases again as compared to derivative **11**.

As expected, binding constants of the spacer-chromoionophores **19a**–**c** and **20** are with both sodium and potassium ions by orders of magnitude larger as compared to **5a** and **9a**. Due to the interrupted conjugation, the ligand nitrogen atoms can participate at the complexation, too, and complexes become more stable. Moreover, the synthesized spacer-chromoionophores provide even better binding properties than the unsubstituted parent aza-crowns. The alkyl side-arm seems to favor the complexation ability as previously reported by other authors for non-chromogenic lariat aza-crown ethers [12–14]. In that case, the relationship between crown cavity size and cation diameter becomes clear because aza-15-crown-5 derivatives **19a**–**c** provide with Na^+ about ten times larger constants than with K^+. The chromophoric aza-18-crown-6 derivative **20** gives with K^+ a larger constant than with Na^+ (Table 1).

Table 1 Complexation constants of the 1:1 complexes of the chromoionophores **9a** with Na^+ and K^+, **9b** with Na^+, **11** with Na^+ and K^+, and **12** with Na^+, and of the spacer-chromoionophores **19a**, **19c**, and **20** with Na^+ and K^+ in [D_6]acetone.

Ligand	K_c (Na^+) ($l \cdot mol^{-1}$)	K_c (K^+) ($l \cdot mol^{-1}$)
9a	310	50
9b	160	
11	3400	3700
12	610	
19a	12000	1200
19c	17000	1200
20	28000	62000

With the synthesized spacer-chromoionophores, crown ether derivatives having very good complexation properties are available, which, on the other hand, are also intensively colored and thus interesting for analytical purposes. UV/Vis absorption spectra of the spacer-chromoionophores are not influenced by complexation with sodium and potassium ions.

Experimental

IR: Perkin-Elmer 298. – UV/Vis: Perkin-Elmer Hitachi 200. – ^{1}H NMR: Bruker 360 and Varian LX 200. For the ^{1}H NMR-spectroscopic determination of the complexation constants [21] the ligands were dissolved in [D_6]acetone ($c = 5 \times 10^{-3}$ $mol \cdot l^{-1}$) and different amounts of a NaSCN or KSCN solution ($c = 5 \times 10^{-2}$ $mol \cdot l^{-1}$) were added. The ^{1}H NMR spectra were recorded after each addition of salt solution.

2-[4-(1,4,7,10-Tetraoxa-13-aza-13-cyclopentadecyl) phenylmethylene] malononitrile (**4**)

0.64 g (2 mmol) of 4-(1,4,7,10-tetraoxa-13-aza-13-cyclopentadecyl)-benzaldehyde **2** and 0.132 g (2 mmol) of malononitrile were dissolved in 3 ml of absolute ethanol, a drop of piperidine was added, and the solution stirred for 30 min at 85 °C. After cooling to room temperature, a dark yellow precipitate was formed which was filtered off. Yellow needles from ligroin, 0.23 g (31%), *m.p.* 150–152°C. – IR (KBr/cm^{-1}) = 2880, 2220, 1610, 1570, 1520, 1440, 1200. – UV-Vis (CH_3OH): λ_{max} (lg ε) = 429 nm (4.75). – ^{1}H NMR ($CDCl_3$): δ/ppm = 3.6–3.8 (m, 20H; crown-H), 6.7 (d, 2H; aromatic-H), 7.45 (s, 1H; olefinic-H), 7.8 (d, 2H; aromatic-H).

$C_{20}H_{25}N_3O_4$	Calcd.:	C 64.67	H 6.78	N 11.31
(371.4)	Found:	C 64.52	H 6.81	N 11.17.

2-Amino-4-[4-(1,4,7,10-tetraoxa-13-aza-13-cyclopentadecyl)phenyl]-1,3-butadiene-1,1,3-tricarbonitrile (**5a**)

0.64 g (2 mmol) of 4-(1,4,7,10-tetraoxa-13-aza-13-cyclopentadecyl)-benzaldehyde **2** and 0.26 g (2 mmol) of 2-amino-1,1,3-tricyano-1-propene were dissolved in 3 ml of absolute ethanol, a drop of piperidine was added, and the solution stirred for 30 min at 85 °C. After cooling to room temperature, the precipitate formed was filtered off. Dark-orange crystals from acetonitrile, 0.6 g (68%), *m.p.* 180–182°C. – IR (KBr/cm^{-1}) = 3320, 3200, 2880, 2220, 2200, 1610, 1570, 1520, 1440, 1190. – UV-Vis (CH_3CN): λ_{max} (lg ε) = 430 nm (4.43). – ^{1}H NMR ([D_6]DMSO): δ/ppm = 3.6 (d, crown-H), 3.7 (s, crown-H), 6.9 (d, 2H; aromatic-H), 7.8 (s, 1H; olefinic-H), 7.9 (d, 2H; aromatic-H), 8.8 (s, br, 2H; -NH_2).

$C_{23}H_{27}N_5O_4$	Calcd.:	C 63.14	H 6.22	N 16.00
(437.5)	Found:	C 63.20	H 6.17	N 15.82.

2-Amino-3-[4-(1,4,7,10-tetraoxa-13-aza-13-cyclopentadecyl)phenylimino]-1-propene-1,1,3-tricarbonitrile (**6a**)

0.64 g (2 mmol) of 13-(4-nitrosophenyl)-1,4,7,10-tetraoxa-13-azacyclopentadecane **3** and 0.26 g (2 mmol) of 2-amino-1,1,3-tricyano-1-propene were dissolved in 3 ml of absolute ethanol, a drop of piperidine was added, and the solution stirred for 30 min at room temperature, finally for 30 min at 60 °C. After cooling to room temperature, the precipitate formed was filtered. Dark-violet crystals from acetonitrile, 0.77 g (87%), *m.p.* 180–182 °C. – IR (KBr/cm^{-1}) = 3400, 3300, 2880, 2220, 2200, 1610, 1520, 1440, 1200. – UV-Vis (CH_3CN): λ_{max} (lg ε) = 524 nm (4.74). – ^{1}H NMR ([D_6]DMSO): δ/ppm = 3.55 (d, crown-H), 3.7 (s, crown-H), 6.95 (d, 2H; aromatic-H), 7.8 (d, 2H; aromatic-H), 8.85 (s, br, 2H; -NH_2).

$C_{22}H_{26}N_6O_4$	Calcd.:	C 60.26	H 5.97	N 19.16
(438.5)	Found:	C 60.51	H 5.99	N 19.27.

2-Bis-(ethoxycarbonyl)amino-4-[4-(1,4,7,10-tetraoxa-13-aza-13-cyclopentadecyl) phenyl]-1,3-butadiene-1,1,3-tricarbonitrile (**5b**)

0.44 g (1 mmol) of 2-amino-4-[4-(1,4,7,10-tetraoxa-13-aza-13-cyclopentadecyl) phenyl]-1,3-butadiene-1,1,3-tricarbonitrile **5a** was dissolved in 7 ml of dichloromethane and 1 ml (1 g, 12.6 mmol) of pyridine. Then, 1.33 ml (1.52 g, 14 mmol) of ethyl chloroformate was added dropwise at 0 °C keeping the temperature below 5 °C. Soon a color change from yellow to violet was observed. The reaction mixture was stirred for further 15 min under cooling and for additional 2 h at room temperature. Then, 10 ml of dichloromethane were added, the solution was washed twice with 1N HCl, further with a saturated aqueous $NaHCO_3$ solution to pH = 7, and finally twice with water. The dichloromethane solution was dried over Na_2SO_4 and concentrated *in vacuo*. The violet dye crystallized upon standing. Violet crystals from 1,4-dioxane or benzene, 0.5 g (86%), *m.p.* 122–124 °C. – IR (KBr/cm^{-1}) = 2880, 2220, 1810, 1610, 1500, 1460, 1440, 1190. – UV-Vis (CH_3CN): λ_{max} (lg ε) = 539 nm (4.77). – ^1H NMR ($CDCl_3$): δ/ppm = 1.35 (t, 6H; -CH_3), 3.65 (d, crown-H), 3.8 (m, crown-H), 4.35 (q, 4H; –CH_2–), 6.75 (d, 2H; aromatic-H), 7.7 (s, 1H; olefinic-H), 7.95 (d, 2H; aromatic-H).

$C_{29}H_{35}N_5O_8$	Calcd.:	C 59.88	H 6.06	N 12.04
(581.6)	Found:	C 59.53	H 6.24	N 12.54.

2-Bis-(ethoxycarbonyl)amino-3-[4-(1,4,7,10-tetraoxa-13-aza-13-cyclopentadecyl)phenylimino]-1-propene-1,1,3-tricarbonitrile (**6b**)

0.44 g (1 mmol) of 2-amino-3-[4-(1,4,7,10-tetraoxa-13-aza-13-cyclopentadecyl)phenylimino]-1-propene-1,1,3-tricarbonitrile **6a** was dissolved in 7 ml of dichloromethane and 1 ml (1 g, 12.6 mmol) of pyridine. Then, 1.33 ml (1.52 g, 14 mmol) of ethyl chloroformate was added dropwise at 0 °C keeping the temperature below 5 °C. Immediately a color change from violet to dark blue was observed. The reaction mixture was stirred for further 15 min under cooling and for additional 45 min at room temperature. Then, 10 ml of dichloromethane were added, the solution was washed twice with 1N HCl, further with a saturated aqueous $NaHCO_3$ solution to pH = 7, and finally twice with water. The dichloromethane solution was dried over Na_2SO_4 and concentrated *in vacuo*. The dark-blue product crystallized easily. Greenish-blue brilliant crystals, 0.5 g (86%), *m.p.* 132–134 °C.– IR (KBr/cm^{-1}) = 2880, 2220, 2200, 1810, 1610, 1550, 1520, 1460, 1440, 1170. – UV-Vis (CH_3CN): λ_{max} (lg ε) = 614 nm (4.79). – ^1H NMR ($CDCl_3$): δ/ppm = 1.35 (t, 6H; -CH_3), 3.65 (d, crown-H), 3.8 (s, crown-H), 4.35 (q, 4H; -CH_2-), 6.8 (d, 2H; aromatic-H), 8.00 (d, 2H; aromatic-H).

$C_{28}H_{34}N_6O_8$	Calcd.:	C 57.72	H 5.88	N 14.42
(582.6)	Found:	C 57.78	H 5.76	N 14.13.

2-Amino-4-[4-(1,4,7,10,13-pentaoxa-16-aza-16-cyclooctadecyl)phenyl]-1,3-butadiene-1,1,3-tricarbonitrile (**9a**)

0.73 g (2 mmol) of 4-(1,4,7,10,13-pentaoxa-16-aza-16-cyclooctadecyl)-benzaldehyde **8** and 0.26 g (2 mmol) of 2-amino-1,1,3-tricyano-1-propene were dissolved in 3 ml of absolute ethanol, a catalytic amount of piperidine acetate was added, and the solution stirred for 14 h at 50–60 °C. After cooling the dark yellow precipitate was filtered off. Yellow crystals from tetrahydrofurane or ethyl acetate, 0.36 g (38%), *m.p.* 148–150 °C. – IR (KBr/cm^{-1}) = 3340, 3180, 2880, 2220, 2200, 1610, 1570, 1520, 1440, 1190. – UV-VIS (CH_3CN): λ_{max} (lg ε) = 426 nm (4.55). – ^1H NMR ([D_6] DMSO): δ/ppm = 3.55 (s, crown-H), 3.65 (m, crown-H), 6.9 (d, 2H; aromatic-H), 7.8 (s, 1H; olefinic-H), 7.9 (d, 2H; aroma-tic-H), 8.8 (s, br, 2H; -NH_2).

$C_{25}H_{31}N_5O_5$	Calcd.:	C 62.35	H 6.48	N 14.54
(481.6)	Found:	C 62.29	H 6.92	N 14.48.

2-Bis-(ethoxycarbonyl)amino-4-[4-(1,4,7,10,13-pentaoxa-16-aza-16-cyclooctadecyl)phenyl]-1,3-butadiene-1,1,3-tricarbonitrile (**9b**)

0.24 g (0.5 mmol) of 2-amino-4-[4-(1,4,7,10,13-pentaoxa-16-aza-16-cyclooctadecyl) phenyl]-1,3-butadiene-1,1,3-tricarbonitrile **9a** was dissolved in 3.5 ml of dichloromethane and 0.5 ml (0.5 g, 6.3 mmol) of pyridine. Then, 0.67 ml (0.76 g, 7 mmol) of ethyl chloroformate was added dropwise at 0 °C keeping the temperature below 5 °C. Soon a color change from yellow to violet was observed. The reaction mixture was stirred for further 15 min under cooling and for additional 1 h at room temperature. Then, 5 ml of dichloromethane were added, the solution was washed twice with 1N HCl, further with a saturated aqueous $NaHCO_3$ solution to pH = 7, and finally twice with water. The dichloromethane solution was dried over Na_2SO_4 and concentrated *in vacuo*. Dark-violet crystals from benzene, 0.26g (83%), *m.p.* 100–102 °C. – IR (KBr/cm^{-1}) = 2880, 2220, 1810, 1610, 1520, 1460, 1440, 1200. – UV-Vis (CH_3CN): λ_{max} (lg ε) = 541 nm (4.84). – ^1H NMR ([D_6]DMSO): δ/ppm = 1.2(t, 6H; - CH_3), 3.55 (s, crown-H), 3.8 (m, crown-H), 4.3 (q, 4H; -CH_2-), 7.05 (d, 2H; aromatic-H), 7.4 (s, 1H; olefinic-H), 8.05 (d, 2H; aromatic-H).

$C_{31}H_{39}N_5O_9$	Calcd.:	C 59.51	H 6.28	N 11.19
(625.7)	Found:	C 59.17	H 6.14	N 10.84.

2-(2,3,5,6,8,9,11,12-Octahydrobenzo[b][1,4,7,10,13]-pentaoxacyclopentadecin-15-ylmethylene)malononitrile (**11**)

0.1 g (0.33 mmol) of 4'-formylbenzo-1,4,7,10,13-pentaoxacyclopentadecane **10**, 0.022 g (0.33 mmol) of malononitrile, and 0.012 g (0.033 mmol) of CdI_2 were dissolved in 1 ml of absolute ethanol, and the mixture was heated for 30 min at 80 °C. The product precipitated after cooling and was filtered off. Light-yellow crystals from ethanol, 0.07g (62%), *m.p.* 130–132 °C. – UV-Vis (CH_3CN): λ_{max} (lg ε) = 370 nm (4.38). – ^1H NMR ([D_6]DMSO): δ/ppm = 3.6 (s, 8H; crown-H), 3.75 (m, 4H; crown-H), 4.05–4.15 (m, 4H; crown-H), 7.2 (d, 1H; aromatic-H), 7.62 (d, 1H; aromatic-H), 7.65 (s, 1H; aromatic-H), 8.33 (s, 1H; olefinic-H).

$C_{18}H_{20}N_2O_5$	Calcd.:	C 62.78	H 5.85	N 8.14
(344.4)	Found:	C 62.43	H 5.89	N 8.14.

2-Amino-4-(2,3,5,6,8,9,11,12-octahydrobenzo[b][1,4,7,10,13]-pentaoxacyclopentadecin-15-yl)-1,3-butadiene-1,1,3-tricarbonitrile (**12**)

0.2 g (0.67 mmol) of 4'-formylbenzo-1,4,7,10,13-pentaoxacyclopentadecane **10**, 0.09 g (0.33 mmol) of 2-amino-1,1,3-tricyano-1-propene, and 0.012 g (0.032 mmol) of CdI_2 were dissolved in 1.5 ml of absolute ethanol and heated for 2 h under reflux. The light-yellow product started to precipitate after 1 h. After cooling the product was filtered off and washed

with a small amount of ethanol. Light-yellow crystals from acetonitrile, 0.17 g (63%), *m.p.* 214–216 °C. – UV-Vis (CH_3CN): λ_{max} (lg ε) = 360 nm (4.26). – ^{1}H NMR ([D_6] DMSO): δ/ppm = 3.65 (s, 8H; crown-H), 3.85 (m, 4H; crown-H), 4.1–4.2 (m, 4H; crown-H), 7.2 (d, 1H; aromatic-H), 7.62 (d, 1H; aromatic-H), 7.66 (s, 1H; aromatic-H), 7.95 (s, 1H; olefinic-H), 9.05 (s, br, 2H; -NH_2).

$C_{21}H_{22}N_4O_5$	Calcd.:	C 61.45	H 5.40	N 13.65
(410.4)	Found:	C 61.60	H 5.37	N 13.84.

Synthesis of the Spacer Crown Ethers (15a–c) and (16a–c) (General Procedure)

0.75 g (3.4 mmol) of 1,4,7,10-tetraoxa-13-azacyclopentadecane **13a** or 0.89 g (3.4 mmol) of 1,4,7,10,13-pentaoxa-16-azacyclooctadecane **13b**, 3.4 mmol of *N*-(*ω*-chloroalkyl)-*N*-alkylaniline **14a–c**, and 0.73 g (6.8 mmol) of sodium carbonate were suspended in 3 ml of absolute ethanol, and the mixture was heated under reflux for 40 h. After cooling the solution was filtered, and the precipitate washed with 15 ml of dichloromethane. The filtrate was concentrated, the residue dissolved in 15 ml of dichloromethane, and washed twice with water. The organic solution was dried over Na_2SO_4 and concentrated *in vacuo* to give a clear, pale yellow oil. The crude products were purified by column chromatography on silica gel 60 using acetone:methanol 3:1 as eluent. Pale yellow, viscous oil, yield: 40–58% for **15a–c** and 37–50% for **16a–c**.

13-[2-(N-Methyl-N-phenyl)-aminoethyl]-1,4,7,10-tetraoxa-13-azacyclopentadecane (**15a**)

Pale yellow, viscous oil, yield: 58%. – ^{1}H NMR ($CDCl_3$): δ/ppm = 2.75 (t, 2H; -CH_2–), 2.82 (t, 4H; crown-H), 2.95 (s, 3H; N–CH_3), 3.45 (t, 2H; -CH_2–), 3.68 (m, 16H; crown-H), 6.7 (m, 3H; aromatic-H), 7.7 (t, 2H; aromatic-H).

$C_{19}H_{32}N_2O_4$	Calcd.:	C 64.74	H 9.15	N 7.95
(352.5)	Found:	C 64.66	H 9.21	N 7.92.

13-[2-(N-Ethyl-N-phenyl)-aminoethyl]-1,4,7,10-tetraoxa-13-azacyclopentadecane (**15b**)

Pale yellow, viscous oil, yield: 40%. – ^{1}H NMR ($CDCl_3$): δ/ppm = 1.15 (t, 3H; -CH_3), 2.72 (t, 2H; -CH_2^-), 2.83 (t, 4H; crown-H), 3.37 (q, 2H; -CH_2–), 3.41 (t, 2H; -CH_2^-), 3.67 (m, 16H; crown-H), 6.63 (t, 1H; aromatic-H), 6.67 (d, 2H; aromatic-H), 7.2 (t, 2H; aromatic-H).

$C_{20}H_{34}N_2O_4$	Calcd.:	C 65.54	H 9.35	N 7.64
(366.5)	Found:	C 65.18	H 9.11	N 7.49.

13-[3-(N-Ethyl-N-phenyl)-aminopropyl]-1,4,7,10-tetraoxa-13-azacyclopentadecane (**15c**)

Pale yellow, viscous oil, yield: 48%. – ^{1}H NMR ($CDCl_3$): δ/ppm =1.15 (t, 3H; -CH_3), 1.78 (m, 2H; -CH_2–), 2.6 (t, 2H; -CH_2^-), 2.8 (t, 4H; crown-H), 3.35 (m, 4H; -CH_2–), 3.65 (m, 16H; crown-H), 6.7 (m, 3H; aromatic-H), 7.7 (t, 2H; aromatic-H).

$C_{21}H_{36}N_2O_4$	Calcd.:	C 66.24	H 9.54	N 7.36
(380.5)	Found:	C 65.92	H 9.49	N 7.38.

16-[2-(N-Methyl-N-phenyl)-aminoethyl]-1,4,7,10,13-pentaoxa-16-azacyclooctadecane (**16a**)

Yellow, viscous oil, yield: 50%. – ^{1}H NMR ($CDCl_3$, 360 MHz): δ/ppm = 2.72 (t, 2H; -CH_2–), 2.83 (t, 4H; crown-H), 2.95 (s, 3H; N–CH_3), 3.45 (t, 2H; -CH_2^-), 3.68 (m, 20H; crown-H), 6.68 (t, 1H; aromatic-H), 6.7 (d, 2H; aromatic-H), 7.2 (t, 2H; aromatic-H).

$C_{21}H_{36}N_2O_5$	Calcd.:	C 63.61	H 9.15	N 7.07
(396.5)	Found:	C 63.17	H 9.05	N 6.72.

16-[2-(N-Ethyl-N-phenyl)-aminoethyl]-1,4,7,10,13-pentaoxa-16-azacyclooctadecane (**16b**)

Yellow, viscous oil, yield: 43%. – ^{1}H NMR ($CDCl_3$, 360 MHz): δ/ppm = 1.15 (t, 3H; -CH_3), 2.72 (t, 2H; -CH_2–), 2.85 (t, 4H; crown-H), 3.37–3.4 (m, 4H; -CH_2^-), 3.68 (m, 20H; crown-H), 6.63 (t, 1H; aromatic-H), 6.67 (d, 2H; aromatic-H), 7.2 (t, 2H; aromatic-H).

$C_{22}H_{38}N_2O_5$	Calcd.:	C 64.36	H 9.33	N 6.82
(410.5)	Found:	C 63.98	H 9.35	N 6.54.

16-[3-(N-Ethyl-N-phenyl)-aminopropyl]-1,4,7,10,13-pentaoxa-16-azacyclooctadecane (**16c**)

Yellow, viscous oil, yield: 37%. – ^{1}H NMR ($CDCl_3$, 360 MHz): δ/ppm = 1.15 (t, 3H; -CH_3), 1.75 (m, 2H; -CH_2–), 2.58 (t, 2H; -CH_2–), 2.78 (t, 4H; crown-H), 3.3 (t, 2H; -CH_2–), 3.38 (q, 2H; -CH_2–), 3.65 (m, 20H; crown-H), 6.63 (t, 1H; aromatic-H), 6.67 (d, 2H; aromatic-H), 7.2 (t, 2H; aromatic-H).

$C_{23}H_{40}N_2O_5$	Calcd.:	C 65.06	H 9.49	N 6.59
(424.6)	Found:	C 65.12	H 9.49	N 6.50.

Synthesis of the Spacer Crown Ether Aldehydes (17a–c) and (18a–c) (General Procedure)

1.3 mmol of 13-[*ω*-(*N*-alkyl-*N*-phenyl)-aminoalkyl]-1,4,7,10-tetraoxa-13-azacyclopenta-decane **15a–c** or 16-[*ω*-(*N*-alkyl-*N*-phenyl)-aminoalkyl]-1,4,7,10,13-pentaoxa-16-azacyclooctadecane **16a–c** was dissolved in 0.5 ml (0.48 g, 6.6 mmol) of *N*,*N*-dimethylformamide and cooled to –10 °C. Then 0.14 ml (0.24 g, 1.56 mmol) of phosphorus oxytrichloride was slowly added keeping the temperature below 0 °C. The reaction mixture was stirred for 15 min under cooling, 1.5 h at room temperature, and finally heated for 4 h at 80 °C. The mixture was left overnight at room temperature, then quenched with water, stirred for 1/2 h, and neutralized with aqueous 40% NaOH solution. The mixture was extracted three times with 10 ml of dichloromethane, and the organic solution was dried over Na_2SO_4. The solvent was removed *in vacuo*, and the obtained dark-yellow oil was further purified by column chromatography on silica gel 60 using acetone as eluent. Yellow oil, yield: 60–71% for **17a–c** and 39–57% for **18a–c**.

4-[N-Methyl-N-2-(1,4,7,10-tetraoxa-13-aza-13-cyclopentadecyl)-ethylamino]-benzaldehyde (**17a**)

Yellow oil, yield: 60%. – ^{1}H NMR ($CDCl_3$): δ/ppm = 2.75 (t, 2H; -CH_2^-), 2.8 (t, 4H; crown-H), 3.1 (s, 3H; N–CH_3), 3.55–3.65 (m, 18H; -CH_2– and crown-H), 6.7 (d, 2H; aromatic-H), 7.7 (d, 2H; aromatic-H), 9.7 (s, 1H; aldehyde-H).

$C_{20}H_{32}N_2O_5$	Calcd.:	C 63.13	H 8.48	N 7.36
(380.5)	Found:	C 63.01	H 8.29	N 7.08.

4-[N-Ethyl-N-2-(1,4,7,10-tetraoxa-13-aza-13-cyclopentadecyl)-ethylamino]-benzaldehyde (**17b**)

Yellow, viscous oil, yield: 68%. – ^{1}H NMR ($CDCl_3$): δ/ppm = 1.18 (t, 3H; -CH_3), 2.72 (t, 2H; -CH_2^-), 2.83 (t, 4H; crown-H), 3.45 (m, 4H; -CH_2–), 3.67 (m, 16H; crown-H), 6.65 (d, 2H; aromatic-H), 7.7 (d, 2H; aromatic-H), 9.7 (s, 1H;

aldehyde-H).

$C_{21}H_{34}N_2O_5$	Calcd.:	C 63.93	H 8.69	N 7.10
(394.5)	Found:	C 64.25	H 8.57	N 6.85.

4-[N-Ethyl-N-3-(1,4,7,10-tetraoxa-13-aza-13-cyclopentadecyl)-propylamino]-benzaldehyde (**17c**)

Yellow, viscous oil, yield: 71%. – ^{1}H NMR ($CDCl_3$): δ/ppm = 1.2 (t, 3H; -CH_3), 1.78 (m, 2H; -CH_2–), 2.58 (t, 2H; -CH_2–), 2.75 (t, 4H; crown-H), 3.45 (m, 4H; -CH_2–), 3.65 (m, 16H; crown-H), 6.7 (d, 2H; aromatic-H), 7.7 (d, 2H; aromatic-H), 9.7 (s, 1H; aldehyde-H).

$C_{22}H_{36}N_2O_5$	Calcd.:	C 64.68	H 8.88	N 6.86
(408.5)	Found:	C 64.28	H 8.72	N 6.59.

4-[N-Methyl-N-2-(1,4,7,10,13-pentaoxa-16-aza-16-cyclooctadecyl)-ethylamino]-benzaldehyde (**18a**)

Yellow, viscous oil, yield: 57%. – ^{1}H NMR ($CDCl_3$, 360 MHz): δ/ppm = 2.78 (t, 2H; -CH_2–), 2.82 (t, 4H; crown-H), 3.1 (s, 3H; N–CH_3), 3.55–3.65 (m, 22H; -CH_2– and crown-H), 6.7 (d, 2H; aromatic-H), 7.7 (d, 2H; aromatic-H), 9.7 (s, 1H; aldehyde-H).

$C_{22}H_{36}N_2O_6$	Calcd.:	C 62.24	H 8.55	N 6.60
(424.5)	Found:	C 61.90	H 8.17	N 6.15.

4-[N-Ethyl-N-2-(1,4,7,10,13-pentaoxa-16-aza-16-cyclooctadecyl)-ethylamino]-benzaldehyde (**18b**)

Yellow, viscous oil, yield: 39%. – ^{1}H NMR ($CDCl_3$): δ/ppm = 1.2 (t, 3H; -CH_3), 2.75 (t, 2H; -CH_2–), 2.83 (t, 4H; crown-H), 3.48 (m, 4H; -CH_2–), 3.65 (m, 20H; crown-H), 6.7 (d, 2H; aromatic-H), 7.7 (d, 2H; aromatic-H), 9.7 (s, 1H; aldehyde-H).

$C_{23}H_{38}N_2O_6$	Calcd.:	C 62.99	H 8.73	N 6.39
(438.6)	Found:	C 62.51	H 8.59	N 6.03.

4-[N-Ethyl-N-3-(1,4,7,10,13-pentaoxa-16-aza-16-cyclooctadecyl)-propylamino]-benzaldehyde (**18c**)

Yellow, viscous oil, yield: 56%. – ^{1}H NMR ($CDCl_3$): δ/ppm = 1.2 (t, 3H; -CH_3), 1.78 (m, 2H; -CH_2–), 2.6 (t, 2H; -CH_2–), 2.78 (t, 4H; crown-H), 3.43 (m, 4H; -CH_2–), 3.65 (m, 20H; crown-H), 6.7 (d, 2H; aromatic-H), 7.7 (d, 2H; aromatic-H), 9.7 (s, 1H; aldehyde-H).

$C_{24}H_{40}N_2O_6$	Calcd.:	C 63.69	H 8.91	N 6.19
(452.6)	Found:	C 63.79	H 8.47	N 5.96.

2-Amino-4-[4-N-methyl-N-2-(1,4,7,10-tetraoxa-13-aza-13-cyclopentadecyl)-ethylamino-phenyl]-1,3-butadiene-1,1,3-tricarbonitrile (**19a**)

0.25 g (0.66 mmol) of 4-[*N*-methyl-*N*-2-(1,4,7,10-tetraoxa-13-aza-13-cyclopentadecyl)-ethylamino]-benzaldehyde **17a**, 0.09 g (0.66 mmol) of 2-amino-1,1,3-tricyano-1-propene, and 0.024 g (0.066 mmol) of CdI_2 were dissolved in 0.7 ml of absolute ethanol, heated for 3 h at 50 °C, and then the mixture was stirred at room temperature till a yellow product precipitated. A small amount of ethanol was added, the mixture stirred for further 15 min, and the precipitate was filtered off. Orange-yellow crystals from acetonitrile, 0.1 g (31%), *m.p.* 176–178 °C. – UV-Vis (CH_3CN): λ_{max} (lg ε) = 444 nm (4.35). – ^{1}H NMR ([D_6]DMSO, 360 MHz): δ/ppm = 2.67 (m, 6H; -CH_2– and crown-H), 3.08 (s, 3H; N–CH_3), 3.48–3.57 (m, 18H; -CH_2– and crown-H), 6.87 (d, 2H; aromatic-H), 7.75 (s, 1H; olefinic-H), 7.87 (d, 2H; aromatic-H), 8.8 (s, br, 2H; -NH_2).

$C_{26}H_{34}N_6O_4$	Calcd.:	C 63.14	H 6.93	N 16.99
(494.6)	Found:	C 62.85	H 6.76	N 16.99.

2-Amino-4-[4-N-ethyl-N-2-(1,4,7,10-tetraoxa-13-aza-13-cyclopentadecyl)-ethylamino-phenyl]-1,3-butadiene-1,1,3-tricarbonitrile (**19b**)

0.2 g (0.51 mmol) of 4-[*N*-ethyl-*N*-2-(1,4,7,10-tetraoxa-13-aza-13-cyclopentadecyl)-ethylamino]-benzaldehyde **17b**, 0.07 g (0.51 mmol) of 2-amino-1,1,3-tricyano-1-propene, and 0.019 g (0.051 mmol) of CdI_2 were dissolved in 0.6 ml of absolute ethanol. The mixture was heated for 3 h at 50 °C and then stirred at room temperature till a yellow product precipitated. A small amount of ethanol was added, the mixture stirred for further 15 min, and the precipitate was filtered off. Orange-yellow crystals from acetonitrile, 0.1g (38%), *m.p.* 163–165 °C. – UV-Vis (CH_3CN): λ_{max} (lg ε) = 450 nm (4.67). – ^{1}H NMR ([D_6]DMSO): δ/ppm = 1.14 (t, 3H; -CH_3), 2.73 (m, 6H; -CH_2– and crown-H), 3.49–3.54 (m, 16H; crown-H), 6.84 (d, 2H; aromatic-H), 7.75 (s, 1H; olefinic-H), 7.87 (d, 2H; aromatic-H), 8.8 (s, br, 2H; -NH_2).

$C_{27}H_{36}N_6O_4$	Calcd.:	C 63.76	H 7.13	N 16.52
(508.6)	Found:	C 63.40	H 7.03	N 16.34.

2-Amino-4-[4-N-ethyl-N-3-(1,4,7,10-tetraoxa-13-aza-13-cyclopentadecyl)-propylamino-phenyl]-1,3-butadiene-1,1,3-tricarbonitrile (**19c**)

0.32 g (0.78 mmol) of 4-[*N*-ethyl-*N*-3-(1,4,7,10-tetraoxa-13-aza-13-cyclopentadecyl)-propylamino]-benzaldehyde **17c**, 0.1 g (0.78 mmol) of 2-amino-1,1,3-tricyano-1-propene, and 0.03 g (0.078 mmol) of CdI_2 were dissolved in 0.6 ml of absolute ethanol, and the mixture was heated for 2 h at 45 °C. After cooling to room temperature an orange-yellow product precipitated. A small amount of ethanol was added, the mixture stirred for 5 min, and the precipitate was filtered off. Orange-yellow crystals from acetonitrile, 0.2 g (50%), *m.p.* 148–150 °C. – UV-Vis (CH_3CN): λ_{max} (lg ε) = 452 nm (4.59). – ^{1}H NMR ([D_6]DMSO, 360 MHz): δ/ppm = 1.15 (t, 2H; -CH_3), 1.68 (m, 2H; -CH_2–), 2.62 (t, 6H; -CH_2– and crown-H), 3.45–3.55 (m, 20H; crown-H), 6.9 (d, 2H; aromatic-H), 7.75 (s, 1H; olefinic-H), 7.9 (d, 2H; aromatic-H), 8.75 (s, br, 2H; -NH_2).

$C_{28}H_{38}N_6O_4$	Calcd.:	C 64.35	H 7.33	N 16.08
(522.6)	Found:	C 64.00	H 7.26	N 16.13.

2-Amino-4-[4-N-ethyl-N-2-(1,4,7,10,13-pentaoxa-16-aza-16-cyclooctadecyl)-ethylaminophenyl]-1,3-butadiene-1,1,3-tricarbonitrile (**20**)

0.14 g (0.32 mmol) of 4-[*N*-ethyl-*N*-2-(1,4,7,10,13-pentaoxa-16-aza-16-cyclooctadecyl)-ethylamino]-benzaldehyde **18b**, 0.042 g (0.32 mmol) of 2-amino-1,1,3-tricyano-1-propene and 0.012 g (0.032 mmol) of CdI_2 were dissolved in 0.5 ml of absolute ethanol, and the mixture was heated for 3 h at 45 °C. After cooling to room temperature an orange-yellow product precipitated. A small amount of ethanol was added, the mixture stirred for 5 min, and the precipitate was filtered off. Orange-yellow crystals from acetonitrile, 0.7 g (40%), *m.p.* 156–158 °C. – UV-Vis (CH_3CN): λ_{max} (lg ε) = 452 nm (4.51). – ^{1}H NMR ([D_6]acetone): δ/ppm = 0.76 (t, 3H; -CH_3), 2.6–2.8 (m, 6H, -CH_2– and crown-H), 3.58–3.6 (m, 24H; crown-H), 7.15 (d, 2H; aromatic-H), 8.15 (s, 1H, olefinic-H), 8.35 (d, 2H; aromatic-H).

$C_{29}H_{40}N_6O_5$	Calcd.:	C 63.02	H 7.29	N 15.21
(552.7)	Found:	C 62.65	H 7.21	N 15.18.

References

[1] F. Vögtle, Supramolekulare Chemie, 1. Aufl., Teubner, Stuttgart 1989, p. 82
[2] H. Zollinger, Color Chemistry, 2. Aufl. , VCH Verlagsgesellschaft, Weinheim 1987, S. 410
[3] M. Takagi, K. Ueno, Topics Curr. Chem. **1984**, *121*, 39
[4] E. Weber, Kontakte (Darmstadt) **1984**, *1*, 26
[5] A. W. Czarnik, Chemistry & Biology **1995**, *2*, 423
[6] J. P. Dix, F. Vögtle, Chem. Ber. **1980**, *113*, 457
[7] S. Fery-Forgues, M. T. Le Bris, J. P. Guetté, B. Valeur, J. Phys. Chem. **1988**, *92*, 384
[8] S. Fery-Forgues, M. T. Le Bris, J. -C. Mialocq, J. Pouget, W. Rettig, B. Valeur, J. Phys. Chem. **1992**, *96*, 701
[9] J. Bourson, B. Valeur, J. Phys. Chem. **1989**, *93*, 3871
[10] M. V. Alfimov, A. V. Churakov, Y. V. Fedorov, O. A. Fedorova, S. P. Gromov, R. E. Hester, J. A. K. Howard, L. G. Kuz'mina, I. K. Lednev, J. N. Moore, J. Chem. Soc. Perkin Trans. 2 **1997**, 2249
[11] N. Mateeva, L. Antonov, M. Miteva, S. Miteva, Talanta **1996**, *43*, 275
[12] T. Wickstrøm, J. Dale, W. Lund, S. Buøen, Anal. Chim. Acta **1988**, *211*, 223
[13] B. D. White, K. A. Arnold, G. W. Gokel, Tetrahedron Lett. **1981**, *28*, 1749
[14] R. A. Schultz, B. D. White, D. M. Dishong, K. A. Arnold, G. W. Gokel, J. Am. Chem. Soc. **1985**, *107*, 6659
[15] L. J. Vanmaele, U. S. Pat. 5,026,677 (1991); Chem. Abstr. **1991**, *114*, 187742f
[16] E. M. Hyde, B. L. Shaw, I. Shephered, J. Chem. Soc., Dalton Trans. **1978**, 1696
[17] F. Wada, H. Hirayama, H. Namiki, K. Kikukawa, T. Matsuda, Bull. Chem. Soc. Jpn. **1980**, *53*, 1473
[18] D. Prajapati, S. Sandhu, J. Chem. Soc., Perkin Trans. 1 **1993**, 739
[19] A. Lattes, A. Verdier, Bull. Soc. Chim. Fr. **1965**, *7*, 2037
[20] F. L. Bach, Jr. , H. J. Brabander, S. Kushner, J. Am. Chem. Soc. **1957**, *79*, 2221
[21] M. Geringer, H. Sterk, Magn. Reson. Chem. **1989**, *27*, 1148
[22] R. M. Izatt, J. S. Bradshaw, S. A. Nielson, J. D. Lamb, J. J. Christensen, Chem. Rev. **1985**, *85*, 271
[23] R. M. Izatt, K. Pawlak, J. S. Bradshaw, R. L. Bruening, Chem. Rev. **1991**, *91*, 1721
[24] R. D. Boss, A. I. Popov, Inorg. Chem. **1986**, *25*, 1747
[25] A. Masuyama, Y. Nakatsuji, I. Ikeda, M. Okahara, Tetrahedron Lett. **1981**, *22*, 4665
[26] A. Boila-Göckel, W. M. F. Fabian, H. Junek, Liebigs Ann. **1996**, 397
[27] A. Boila-Göckel, H. Junek, P. Czerney, J. Prakt. Chem. **1997**, *339*, 742
[28] H. Junek, M. Klade, P. Biza, M. Geringer, H. Sterk, Liebigs Ann. **1990**, 741
[29] R. Trültzsch, J. Beger, G. Wolf, H.-J. Buschmann, J. Prakt. Chem. **1994**, *336*, 5

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