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ORGANIC CHEMOSENSORS WITH CROWN-ETHER GROUPS (REVIEW)

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Recent advances in the chemistry of organic chemosensors containing crown–ether groups are reviewed.

Keywords: crown ethers, chemosensors, fluorescence, photochromism, electronic absorption spectra.

Organic chemosensors are molecules of abiotic nature capable of interacting selectively and irreversibly with a specific substrate (ion, molecule) with corresponding changes in one or more characteristics of the system. A series of reviews have described methods for the synthesis of chemosensors [1] and their use in the determination of metal cations [2-8], anions, and molecules [4, 9, 10]. Some of them treat the various types of fluorescent chemosensors [5-8] or photoswitching compounds [11-14] selectively. In this review, based exclusively on the results of recent years, sensors containing crown-ether groups are examined. Special attention is paid to the various mechanisms of action of crown-containing chemosensors, which are classified according to their electronic and photochemical characteristics.

In the general case a chemosensor molecule consists of signal and receptor parts with a bridge between them although the latter may be absent. As a rule chemosensors can be subdivided into chromogenic, fluorescent, and photoswitchable.

During the interaction of a *chromogenic* sensor with the substrate (in particular with a metal ion) a hypsochromic or bathochromic shift of the long-wave absorption band of the initial compound is observed. If the shift of the bands is significant and takes place in the visible part of the spectrum it leads to a visually discernable change in the color of the solution. Such signal systems are usually called colorimetric or "naked-eye" chemosensors.

The action of *fluorescent* chemosensors is based both on change of the fluorescence intensity and on shift of the emission band of the initial compounds during the formation of a complex with the substrate.

Photoswitchable chemosensors are capable of reversible "switching on–switching off" of their sensor characteristics under the influence of light.

Among ionophore–receptors capable of combining with positively charged ions, it is possible to include chelating agents, podands, coronands (or crown ethers), cryptands, calixarenes, cyclodextrins, etc. [15].

Crown ethers, discovered by Pedersen in 1962, occupy a special position among receptors and are widely used in the design of new chemosensors based on their unique ability to combine with the cations of alkali metals, their fairly high selectivity, and their accessibility. In addition to alkali metals, crown ethers are also effective complexing reagents for the cations of alkaline-earth metal, Pb^{2+}, and Tl^{2+}, and when nitrogen and sulfur atoms are inserted into their structure they become sensitive to Ag^{+}, Hg^{2+}, and Cd^{2+} ions. The

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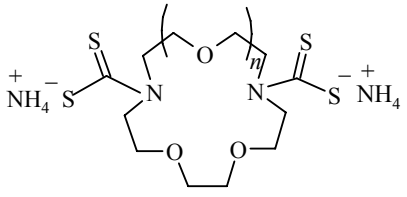
detection of these ions in biological liquids and the environment is particularly important in medicine and biology. On the one hand, these cations are involved in various biological processes (Na^+, K^+, Mg^{2+}, Ca^{2+}) and are used in the treatment of various illnesses (Li^+, Ca^{2+}), while on the other hand they can cause serious harm to the environment and to human health (Ba^{2+}, Pb^{2+}, Tl^+, Ag^+, Hg^{2+}, Cd^{2+}). Despite the large number of chemosensors available for the determination of these groups of ions it is extremely important to obtain new compounds that simultaneously combine such qualities as safety, accessibility, sensitivity, and selectivity.

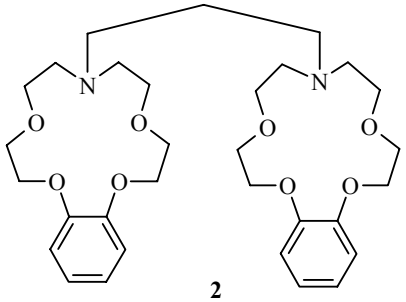
1. CHROMOGENIC SENSORS

The fairly simple system **1a**,**b** is capable of combining with the ions of heavy and transition metals and leads to corresponding changes in the ultraviolet part of the spectrum: During the formation of crown ether complexes with cations (Ni^{2+}, Pd^{2+}, Co^{2+}, Pb^{2+}) a new absorption band appears in the region of 320 nm [16]. The sensor **2** acts in a similar way but with respect to sodium and potassium ions [17]. Interaction with these ions leads to a hypsochromic shift of the long-wave absorption maximum of the compound (λ_{max} ~275 nm).



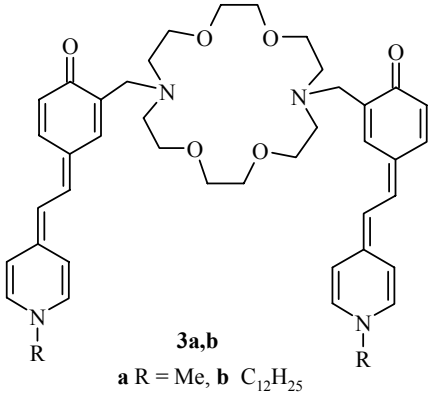
1a,b

a n = 1, **b** n = 2



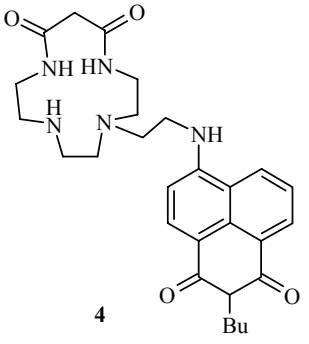
2

However, sensor systems absorbing in the visible region are most often employed [18]. This gives not only higher sensitivity and accuracy in the quantitative analysis of substances but also the possibility of detecting the ions in solution visually. An example is compounds **3a**,**b**, which can be used for the selective detection of Ca^{2+} ions in human blood and plasma [19].



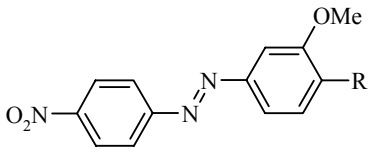
3a,b

a R = Me, **b** $C_{12}H_{25}$

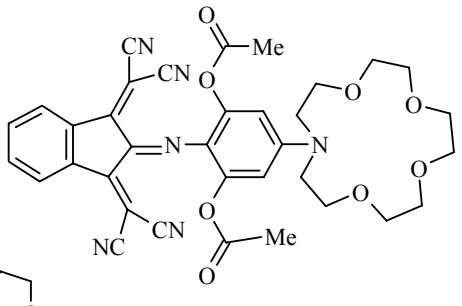


4

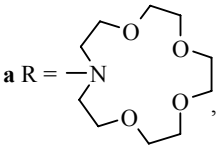
The negatively charged oxygen atoms of the two merocyanine fragments take part in additional coordination with the metal ion, leading to internal charge transfer (the ICT effect). This gives rise to a bathochromic shift of the long-wave absorption band of the initial compounds from 410 to 450 nm and to the build up of fluorescence at 575 nm. The sensors can be used for the quantitative determination of calcium at concentrations $c = 1 \cdot 10^{-5}$-$1 \cdot 10^{-2}$ M even in the presence of a large excess of Mg^{2+}, Li^+, Na^+, and K^+ ions (c_M = 0.1 M).



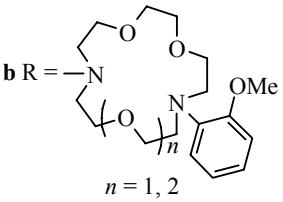
5a,b



6

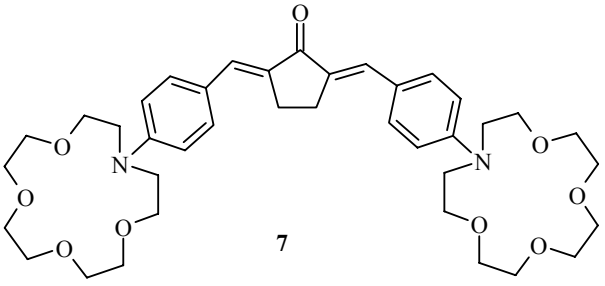


a R =



b R =

n = 1, 2



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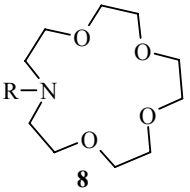

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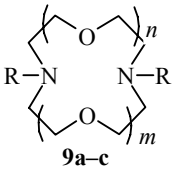
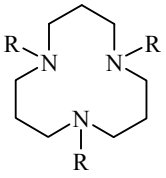


9a–c

a *n* = *m* = 1;
b *n* = 2, *m* = 1;
c *n* = *m* = 2



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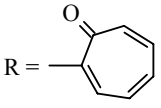
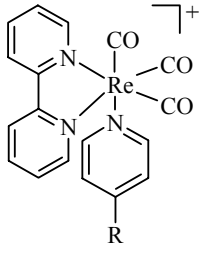
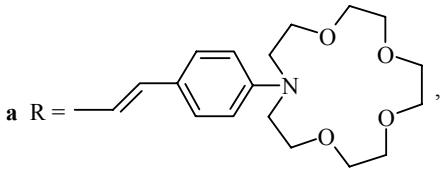
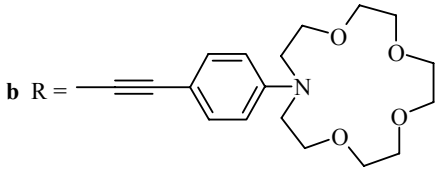




11a,b



a R =

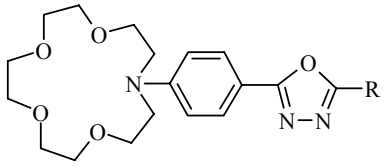


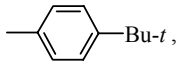
b R =

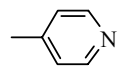
Recently the highly sensitive and highly selective nitrogen-containing naked-eye chemosensor **4** was synthesized [20]. This made it possible to detect copper (c ~$3\cdot10^{-7}$ M) and mercury (c ~$7\cdot10^{-7}$ M) ions in solution qualitatively and quantitatively in the presence of Fe^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Mn^{2+}, Cd^{2+}, Pb^{2+}, Ag^{+}, Na^{+}, K^{+}, and Mg^{2+} cations.

In most of the other chromogenic chemosensors the electron-donating azacrown ether and the accepting chromophore are conjugated with each other and form a single π-electron system, and their action is also based on the ICT effect. The changes occurring in the absorption spectra of the compounds are due to the different

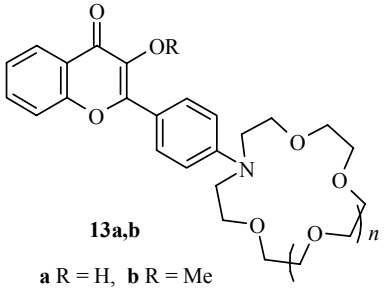
effects of the formation of the crown ether complex on the energy levels of the ground and excited states. Thus, electronic excitation in the donor–acceptor chromoionophores **5a**,**b** [21-23], **6** [24], **7** [25], **8-10** [26], **11a**,**b** [27], **12** [28], **13a**,**b** [29], **14a-c**, and **15** [30] are as a rule accompanied by the transfer of electron density toward the accepting substituents of the chromophore. Interaction of the receptor with the positively charged metal ion therefore destabilizes the excited state to a greater degree than the ground state and leads to a hypsochromic shift of the absorption band.



a R =  Bu-*t*,

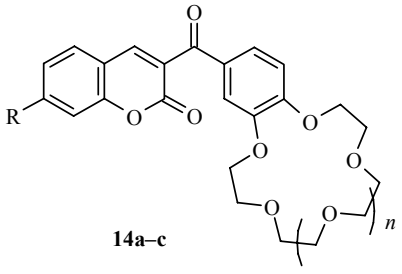
b R = 

12a,b



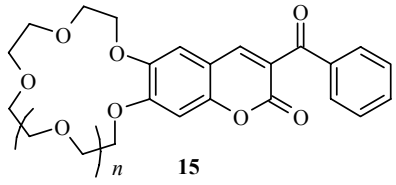
13a,b

a R = H, **b** R = Me



14a–c

a R = H, **b** R = OMe, **c** R = NEt_2

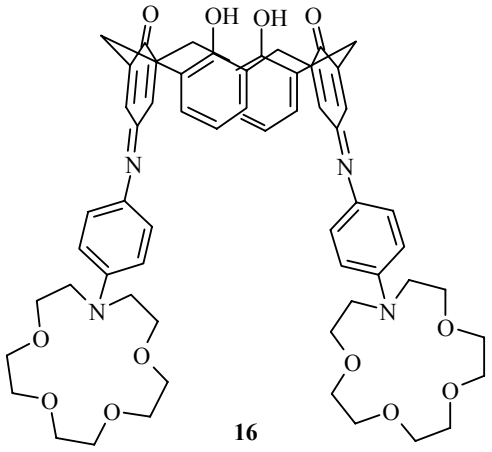


15

13a,b, 14a–c, 15 *n* = 1, 2

The azo dyes **5a**,**b** are effective colorimetric sensors for the selective determination of sodium or potassium ions in blood. During complex formation the hypsochromic shift of the long-wave absorption band in the given compounds (Δλ 110 nm) is accompanied by change of the color of the solution from red to yellow.

The chemosensor systems **6-15** proved sensitive to the presence of the ions of alkali metals (compounds **6**, **11**, **13**), alkaline-earth metals (compounds **7-15**), and certain transition metals (compounds **8-10**) in the solutions.

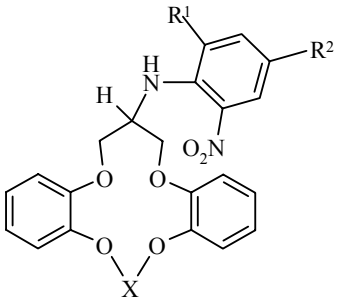


16

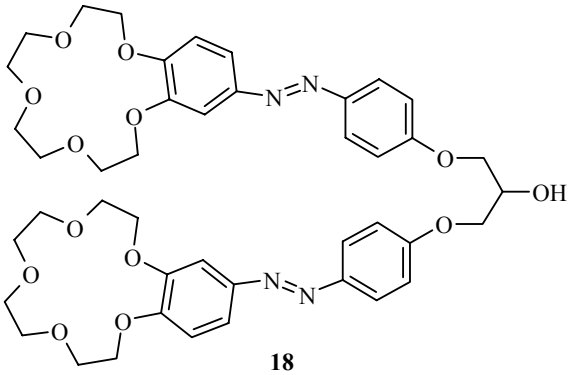
The synthesis and spectral characteristics of the selective ambident sensor **16** [31], containing two receptor parts that simultaneously fulfill the role of donor (azacrown ether) and acceptor (the calixarene part), were described. The Eu^{3+} ions react mainly with the oxygen atoms of the calixarene, whereas the Na^{+} ion combines with the azacrown ether, giving rise to a bathochromic or hypsochromic shift of the absorption bands respectively.

The results from spectral investigations of the series of compounds **17**, containing picrylamine chromophores capable of additional coordination with metal cations, are presented in [32]. During the extraction of sodium, potassium, and lithium salts from an aqueous alkaline solution into a chloroform layer it was found that ionization of the sensor molecules occurs, and one or the other metal cation interacts with the crown ether cavity, leading to the appearance of a new strong absorption band in the visible region.

Compound **18** is highly selective with respect to potassium ions and forms with them an intramolecular "sandwich" structure, appearing in the spectrum as a hypsochromic shift of the long-wave absorption band [33].



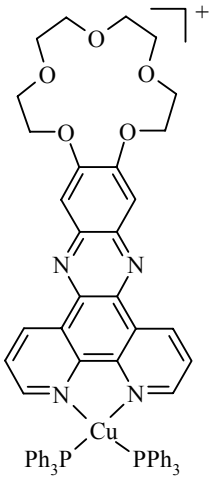
17



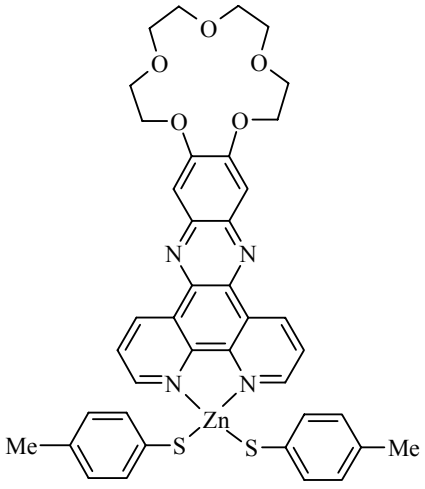
18

17 X = $(CH_2)_3$, $CH_2CH_2OCH_2CH_2$, $CH_2(CH_2OCH_2)_2CH_2$, $R^1 = NO_2, CF_3$; $R^2 = NO_2, CN, CF_3$

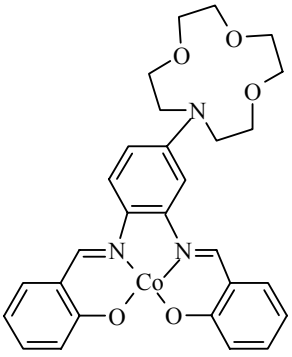
Various chelate complexes **19-22** can also be used as effective sensor systems [34-36].



19a

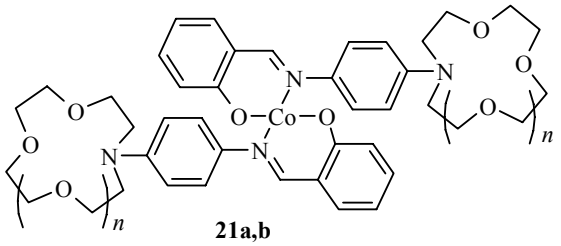


19b



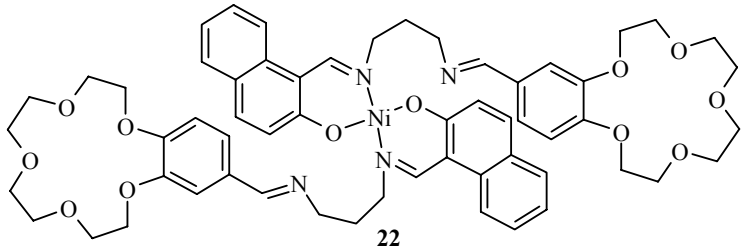
20

The chemistry of ditopic sensors capable of the recognition not only of individual ions but also of complete ion pairs has recently been developing at high rates, and this is of great importance not only in chemistry but also in medicine in so far as the biological activity and pharmaceutical characteristics of the



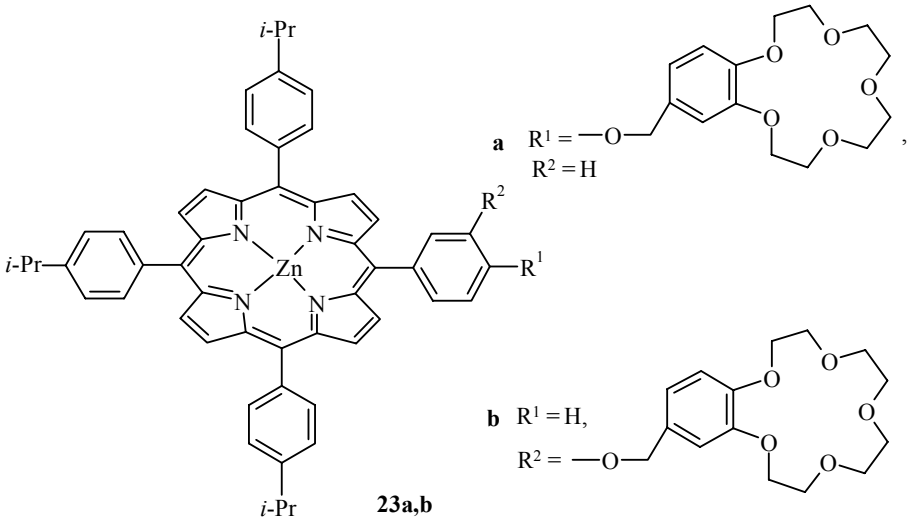
21a,b

a $n = 1$, **b** $n = 2$

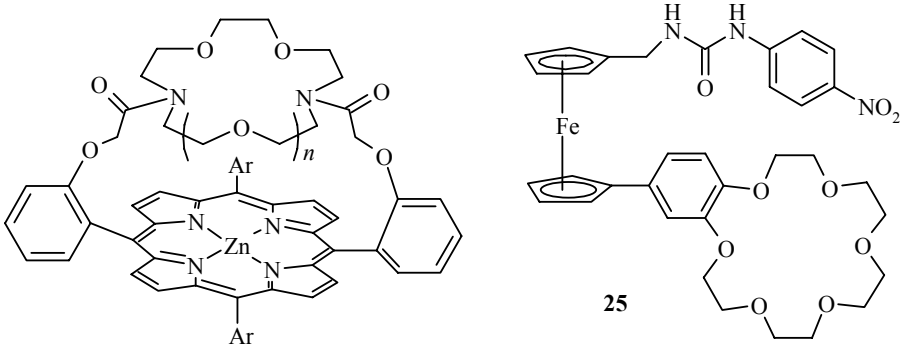


22

ionized molecules often depend on the type of counterion. Thus, compounds **23a**,**b** [37], **24a**,**b** [38], and **25** [39] can be used for the visual detection of toxic salts of alkali metals (NaCN, KCN, KF) in aqueous and organic media. According to data from ^{1}H NMR spectroscopy, the metal cation is held by the crown ether cavity and the counterion by the zinc atom of the porphyrin macrocycle or by the urea fragment respectively.



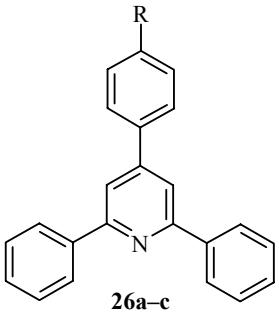
23a,b



24a,**b**

a $n = 1$, **b** $n = 2$

An original ditopic chemosensor system **26** for the selective recognition of a wide range of anions ($MeCOO^-$, F^-, I^-, and CN^-) was presented in [40].



26a–c

a R = NMe_2,

b R =

c R =

,

The complexes of the compounds with Cu^{2+}, Zn^{2+}, Hg^{2+}, Fe^{2+}, and Pb^{2+} cations can be used as "naked-eye" reagents. During their reaction with the anions a different optical response, expressed as a change in the color of the solution, is observed for each anion.

By analyzing this set of data it is possible to determine unambiguously the presence of one or the other anion in the sample being investigated (with the exception of NO_3^-, Cl^-, and Br^- anions, which show similar spectral behavior).

2. FLUORESCENT CHEMOSENSORS

Fluorescence analysis has a number of advantages in comparison with other spectral methods; it is highly sensitive and simple in execution and can be used over a wide range of concentrations of the investigated material. The two main types of fluorescent chemosensors are the PET (photoinduced electron transfer) and ICT systems, although in certain cases it is quite difficult to draw a clear boundary between them. The basic scheme for the action of PET sensors can be represented as follows: During excitation of the molecule an electron from the highest occupied molecular orbital (HOMO) of the receptor transfers to the HOMO of the fluorophore, and this leads to quenching of the fluorescence of the latter. Complex formation with the metal ion leads to the result that the energy level of the HOMO of the receptor becomes lower than the level of the HOMO of the fluorophore, the PET effect does not arise, and the intensity of the fluorescence increases. The structures of some crown-containing PET sensors are given in Table 1.

TABLE 1. Examples of Crown-Containing PET Sensors

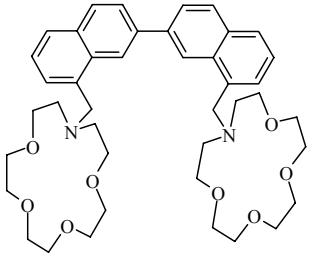
№	Compound	M^{n+}	I/I_0 *	Reference
1	2	3	4	5
27		Ba^{2+}	~7	[41]

TABLE 1 (continued)

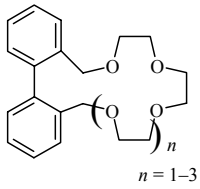
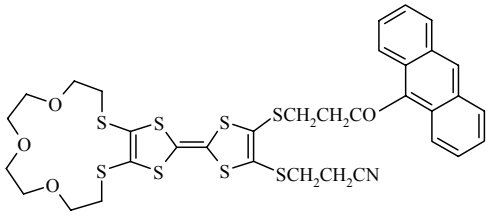
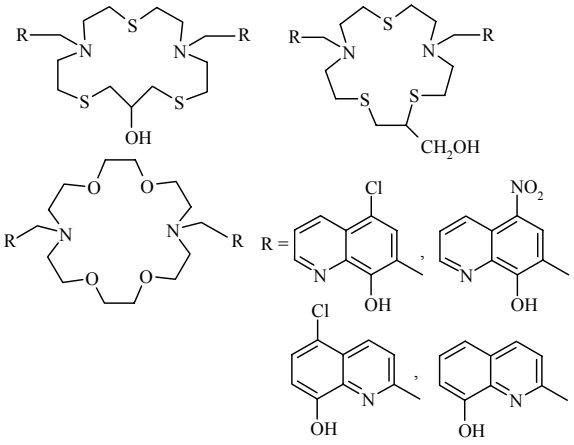
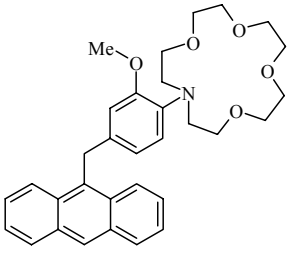
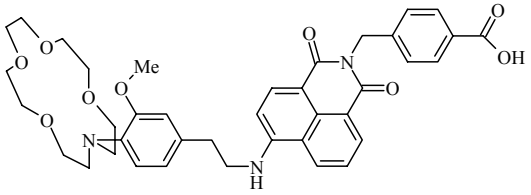
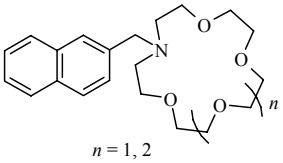
1	2	3	4	5
28	 n = 1–3	Ca^{2+}	4	[42]
29		Li^{+}	1.4	[43]
30		Mg^{2+} Cd^{2+} Hg^{2+}	1000 3 12	[44–48]
31		Na^{+}	5.5	[21]
32		Na^{+}	18	[49]
33	 n = 1, 2	Li+ K+	6 7	[50, 51]

TABLE 1 (continued)

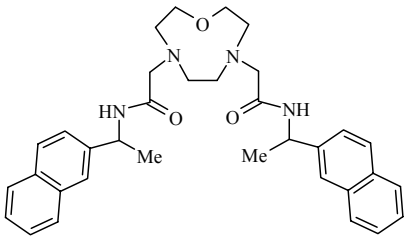
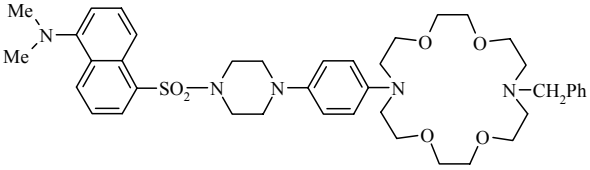
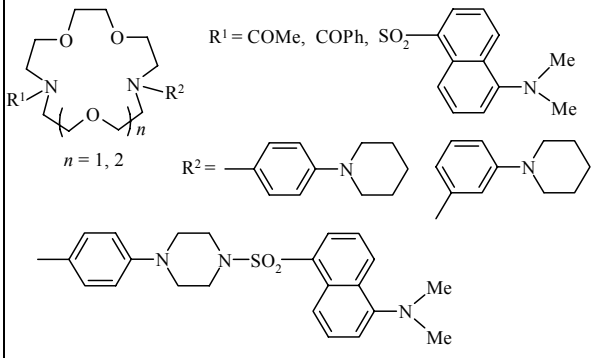
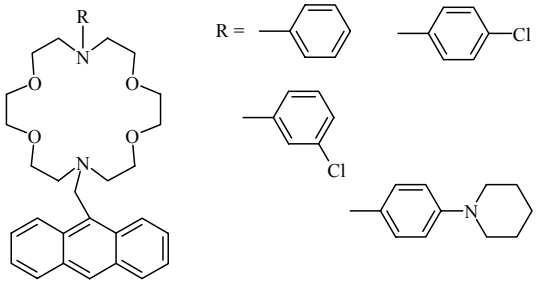
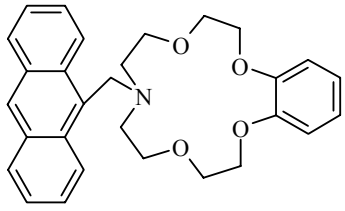
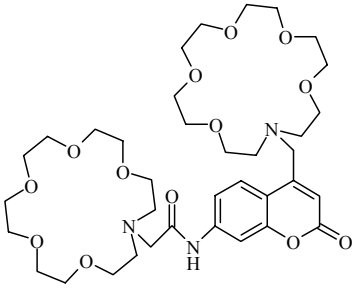
1	2	3	4	5
34		Li^+	-6	[52]
35		Ca^{2+}	-5	[53]
36		Ca^{2+}, Mg^{2+}	3-13	[53]
37		Ca^{2+}	30-170	[54]
38		Zn^{2+}	10	[55]
39		Fe^{3+}	15	[56]

TABLE 1 (continued)

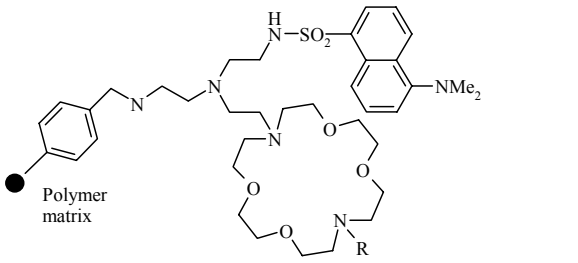
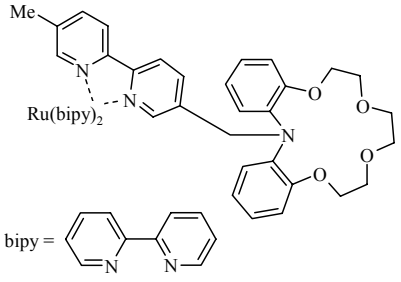
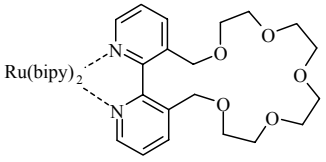
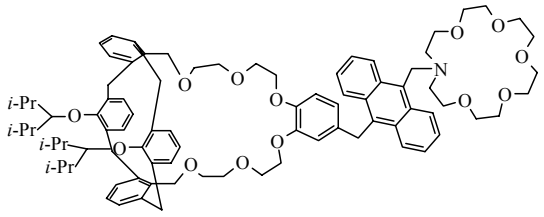
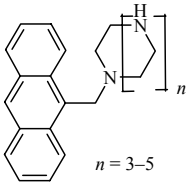
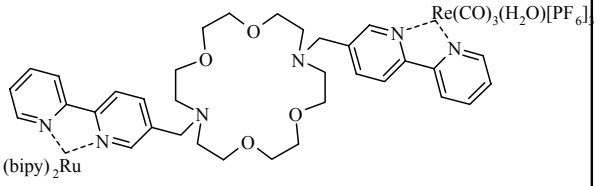
1	2	3	4	5
40		Mg^{2+}	2	[57]
41		Li^{+}	~2	[58]
42		Na^{+}	2.7	[59]
43		Cs^{+} K^{+}	4 7	[60]
44		Cd^{2+}	-25	[61, 62]
45		Ba^{2+}	-2	[63]

TABLE 1 (continued)

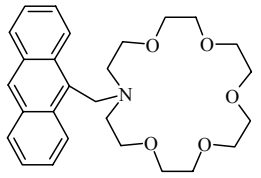
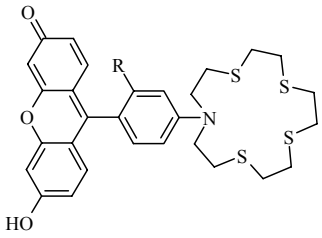
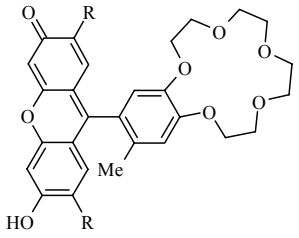
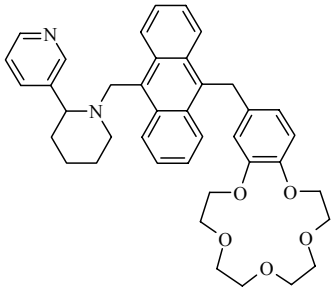
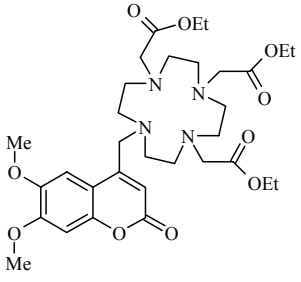
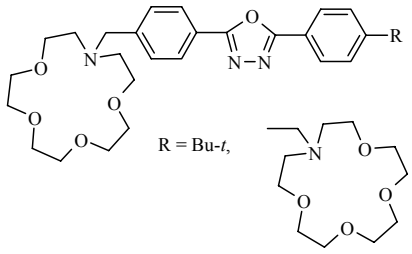
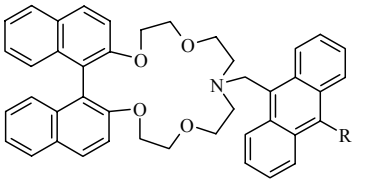
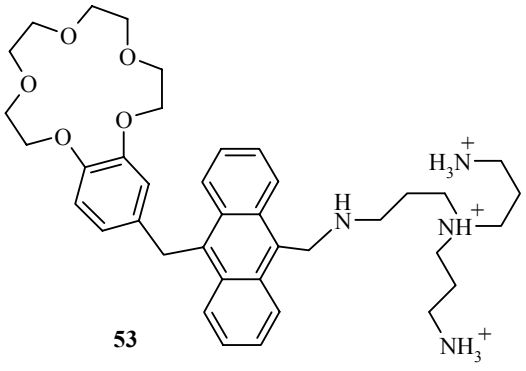
1	2	3	4	5
46		K^+	50	[64]
47	 R = H R = Me	Hg^{2+} Hg^{2+}	170 44	[65, 66]
48	 R = H, Cl	Na^+	5	[67]
49		Na^+	-15	[68]
50		Zn^{2+}	4.4	[69]

TABLE 1 (continued)

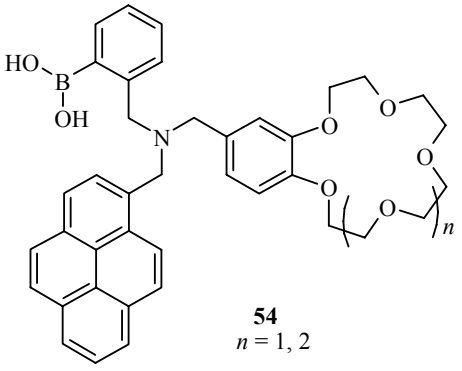
1	2	3	4	5
51	 R = Bu-*t*,	Mg^{2+}	20-24	[70]
52	 R = H, CN	Hg^{2+}	-10	[71]

* I/I_0 is the relative increase of the fluorescence intensity.

Among the PET chemosensors there are also ditopic systems such as compounds **53** [72] and **54** [73], capable of detecting sodium phosphate and potassium fluoride respectively.



53



54
n = 1, 2

More rarely, the so-called CHEQ (chelation enhanced fluorescence quenching) PET sensors, in which fluorescence quenching is observed during the formation of their complexes with metal ions, have been used for analytical purposes. The fluorescence characteristics of the CHEQ system depend not only on the structure of the ligand but also on the electronic structure of the metal ion itself [74, 75].

The second widespread class of luminescent sensors contains the ICS systems, the molecules of which are constructed in such a way that the fluorophore either interacts directly with the metal cation on account of additional coordination or forms a system of conjugated bonds with the receptor. As in the case of chromogenic sensors, the formation of a complex with a cation leads to intramolecular charge transfer and to change in the luminescence-spectral characteristics of the molecule, appearing as a significant hypso- or bathochromic shift of the fluorescence band and, accordingly, a change in the luminescence intensity at the emission wavelength of the complex (Table 2).

TABLE 2 Examples of Crown-Containing ICT Chemosensors

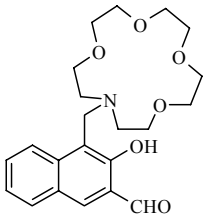
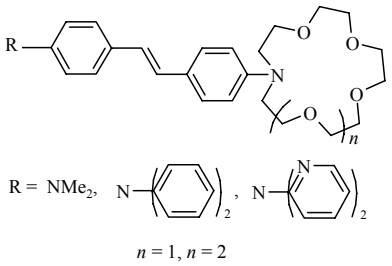
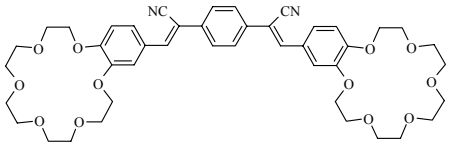
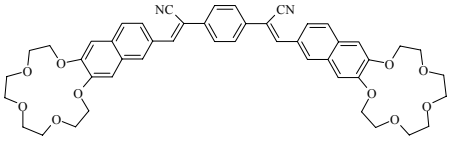
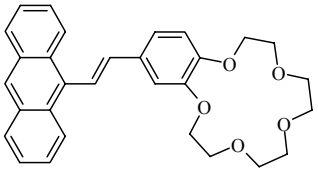
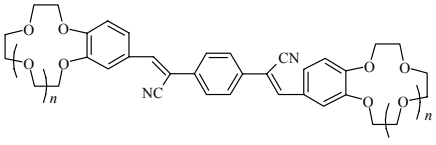
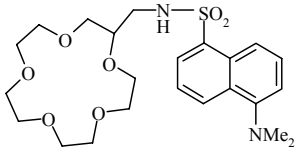
№	Compound	M^{n+}	I/I_0 *	λ_{fl} ($\Delta\lambda$*[2]), nm,	Refe-rence
1	2	3	4	5	6
55		Ca^{2+}	~12	560 (-20)	[76]
56	 R = NMe_2, n = 1, n = 2	Ca^{2+} Ba^{2+}	~2 ~2	425-465 (from -25 to +25)	[77]
57		Cs^+	20	526 (+44)	[78]
58		K^+	27	512 (+34)	[79]
59		Mg^{2+}	17	481 (-20)	[80]
60		Na^+ K^+ Cs^+	20 20 20	537 (+81) 492 (+17) 526 (+44)	[81]
61		Co^{2+}	0.15	~525 (+5)	[82]

TABLE 2 (continued)

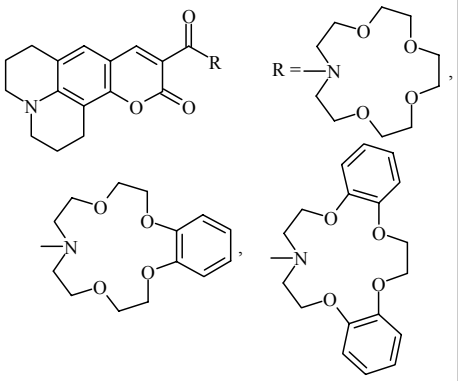
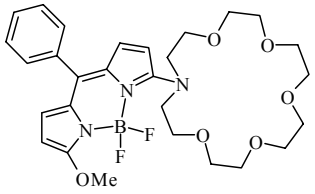
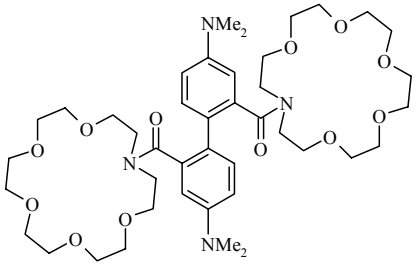
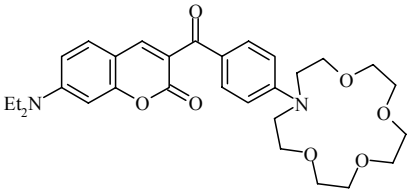
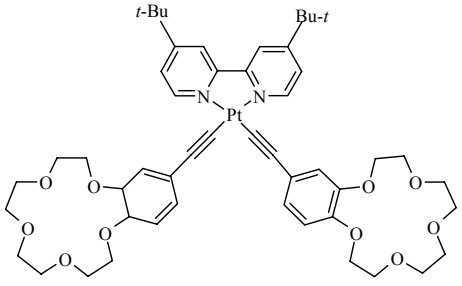
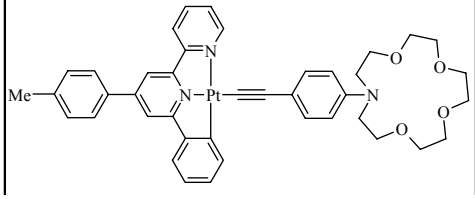
1	2	3	4	5	6
62		Mg^{2+} Ca^{2+}	~ 1 ~ 1	~ 500 (+25) ~ 500 (+23)	[83]
63		K^{+}	~ 35	520(-45)	[84]
64		Zn^{2+} Cd^{2+}	0.24 0.62	491 (+17) 486 (+12)	[85]
65		Pb^{2+}	40	491(+15)	[86]
66		Zn^{2+} Mg^{2+}	870 1035	560 (-75) 553 (-82)	[87]
67		Mg2+	>100	570	[88]

TABLE 2 (continued)

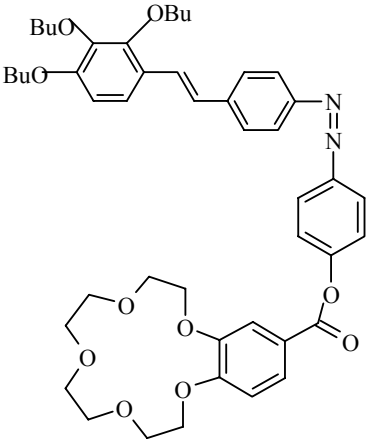
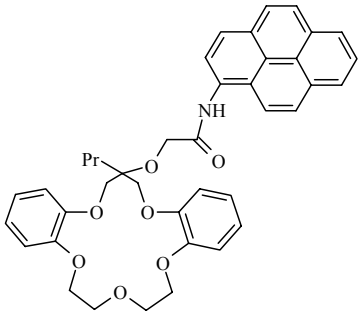
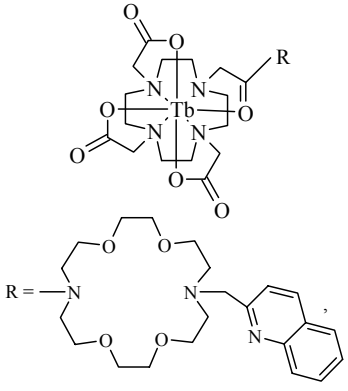
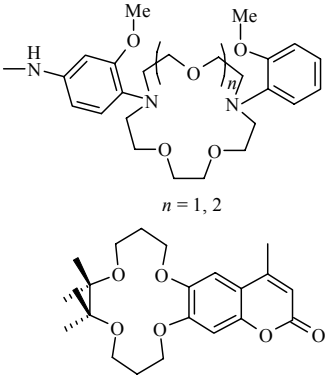
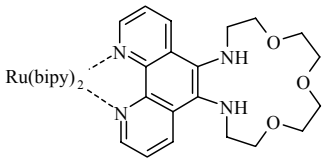
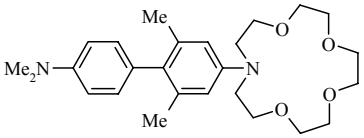
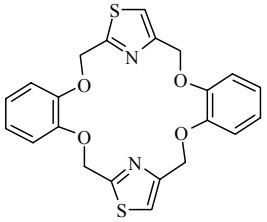
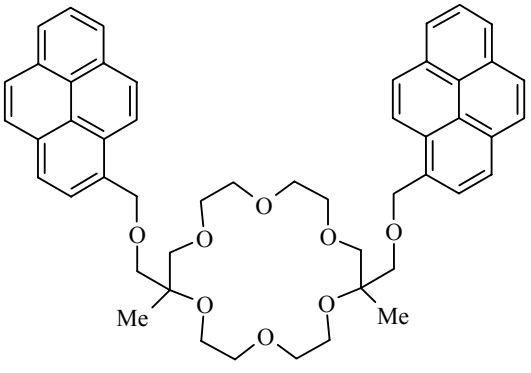
1	2	3	4	5	6
68		Pr^{3+} Nd^{3+} Eu^{3+}	>100 >100 >100	~ 350 ~ 360 ~ 400	[89]
69		Na^{+}	~5	459 (+51)	[90]
70		K^{+}	40	547	[91, 92]
71		Li+	0.5	~ 405 (-20)	[93]

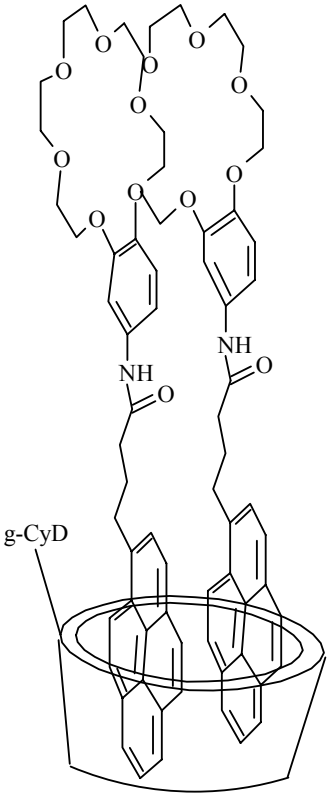
TABLE 2 (continued)

1	2	3	4	5	6
72		Hg^{2+}	8	620 (+10)	[94]
73		Zn^{2+}	~18	420 (+60)	[95]
74		Ag^{+} Pb^{2+} Hg^{2+}	14.5 9.2 7.2	335 (+40) 335 (+40) 335 (+40)	[96]

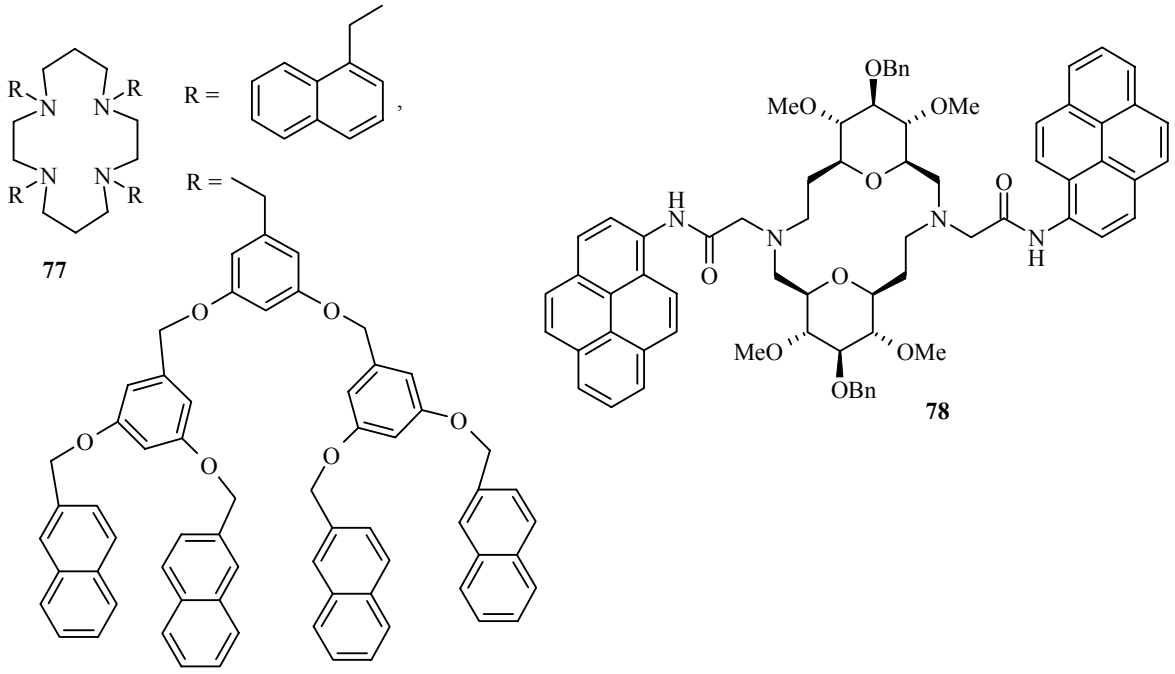
* I/I_0 is the relative increase of the fluorescence intensity.
*[2] The fluorescence maximum after complex formation (hypsochromic (−) and bathochromic (+) shifts of the fluorescence band).



75



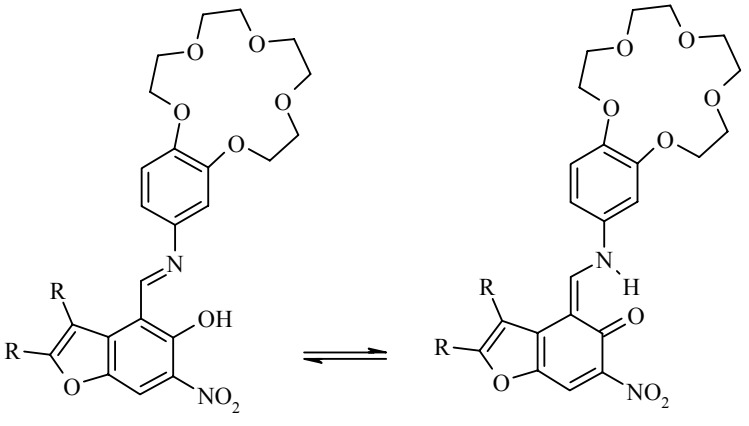
76



Other types of fluorescent chemosensors include monomer-excimer systems such as **75** [97], **76** [98], **77** [99], and **78** [100].

In the excimers the aromatic fragments of the molecule are parallel at the optimum distance and form a "sandwich" structure, which only exists in the excited state. The luminescence bands do not have fine structure and are located in a more long-wave region than the emission maxima of the individual components. The action of this type of sensor is based on the change in the ratio of the excimer and monomer emission in the solution during complex formation with the metal ions.

A new type of fluorescent chemosensors is the tautomeric system that we developed on the basis of benzo-15-crown-6-containing imines of the benzo[*b*]furan series **79** and **80** [101-103]. Their action is based on the displacement of the benzenoid–quinonoid equilibrium toward the benzenoid form during complex formation with the cations of alkali and alkaline-earth metals, accompanied by a significant reduction in the intensity of the long-wave absorption band and a substantial hypsochromic shift of the emission band.



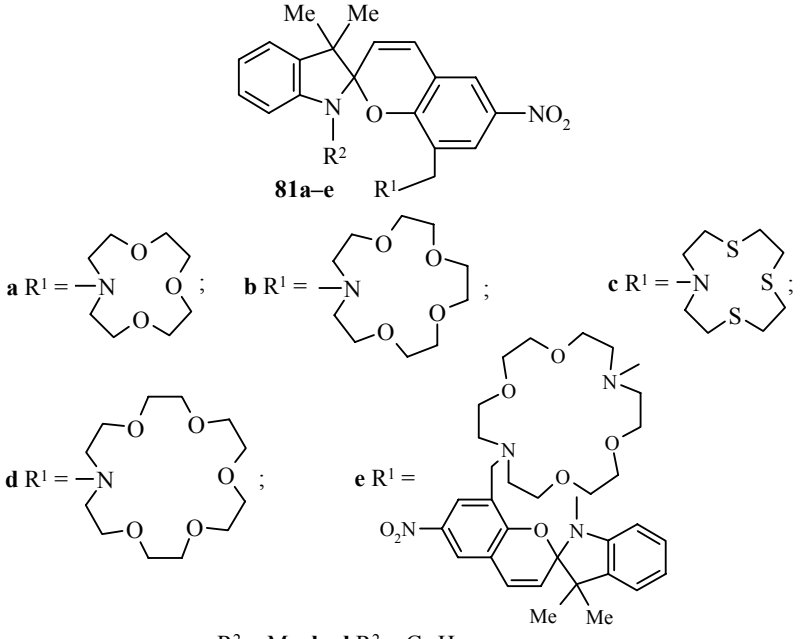
79, 80 A **79, 80 B**

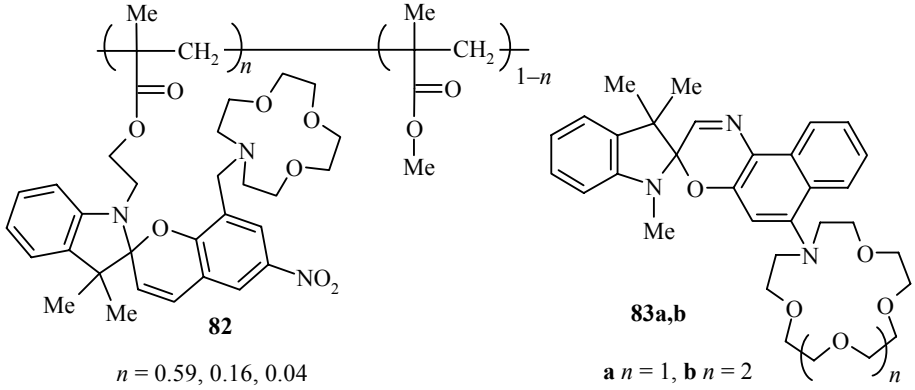
79 R = Ph; **80** R + R = –$(CH_2)_4$–

3. PHOTOSWITCHABLE CHEMOSENSORS

Photochromism is the reversible transformation of a substance from one form to another by the action of electromagnetic radiation [104, 105]. The reversible transformation can be realized both photochemically and thermally. The sensor system can be activated or blocked by means of a photoreaction. Most crown-containing photoswitchable chemosensors are derivatives of spiropyrans, spirooxazines, chromenes, and styryl dyes. (Fulgides [106], dihetarylethenes [107, 108], and triphenylmethane dyes [109, 110] are encountered less frequently.)

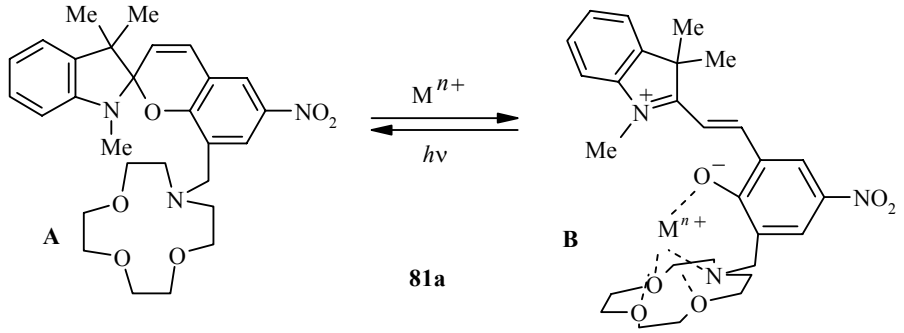
Recently, spiropyrans and spirooxazines of the indoline series **81a-e**, **82**, and **83a**,**b** containing various crown ether receptors were synthesized [111-118].



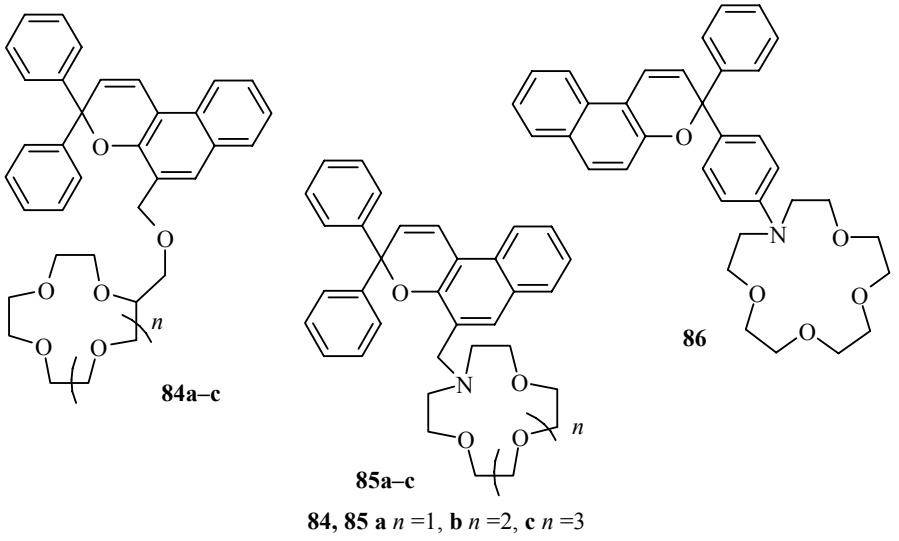


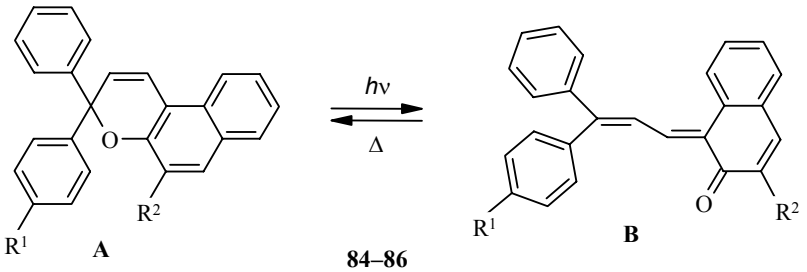
In the presence of the cations of alkali and alkaline-earth metals the spiropyrans **81**-**83** are capable of being transformed into the corresponding merocyanine form, which has absorption in the visible part of the spectrum (λ_{max} ~550 nm). This fact is explained by the ability of the metal ions to form an additional coordination bond with the phenolate anion, stabilizing the merocyanine form **B** of the spiro compound (e.g., in the molecules of **81a**). The process is most effective if the sizes of the crown ether cavity and the metal ion are in the optimum ratio.

Irradiation of the compounds **81** and **82** in the region of the long-wave absorption band of the merocyanine form leads to the formation of the initial spiro form and a released metal ion, making it possible to control the complex formation process by irradiation.



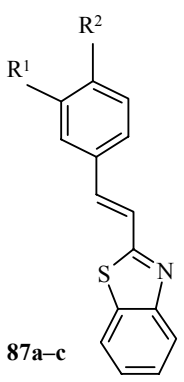
The photochromic reaction of the chromenes **84-86** [119-121] involves cleavage of the C–O bond by the action of light with the formation of the open form **B**. At room temperature the reaction is reversible.



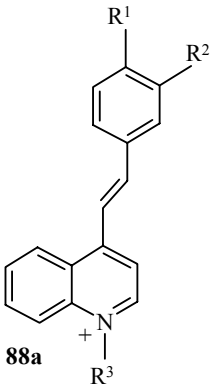


Irradiation of solutions of these compounds in the presence of the ions of alkali and alkaline-earth metals leads to the appearance of a strong absorption maximum in the region of 450-500 nm due to the formation of the open form but leads to a substantial decrease of the rate constant of reverse thermal cyclization as a result of stabilization of form **B** resulting from additional coordination of the metal ion with the carbonyl oxygen atom.

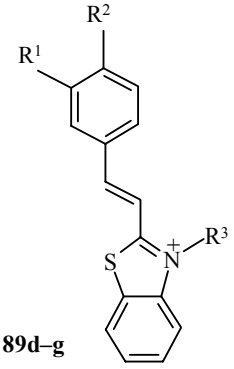
The crown-containing styryl dyes **87-90**, which form molecular dimers in the presence of metal ions, were described in the cycle of papers [122-128]. During irradiation of solutions of the monomers stereospecific photocyclization takes place with the formation of only one or two derivatives of cyclobutane (of the 11 possible derivatives). It was shown that compounds **87-90** do not enter into photocyclization in the absence of the metal ions even in saturated solutions. The metal ion participates in the formation of molecular dimers, fulfilling the role of "molecular glue", thereby promoting the photoreaction. Effective chemosensors for magnesium, barium, mercury, and lead ions have been found among these systems.



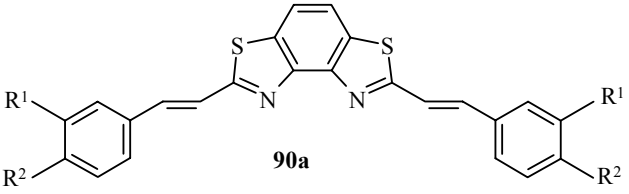
87a–c



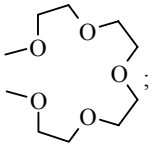
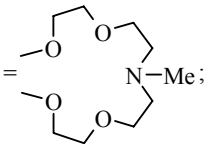
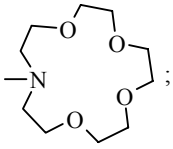
88a

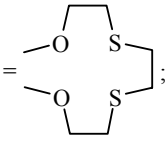
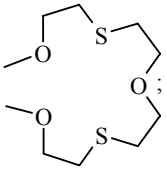
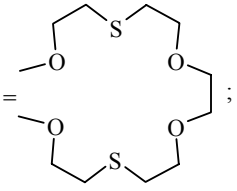


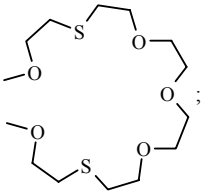
89d–g



90a

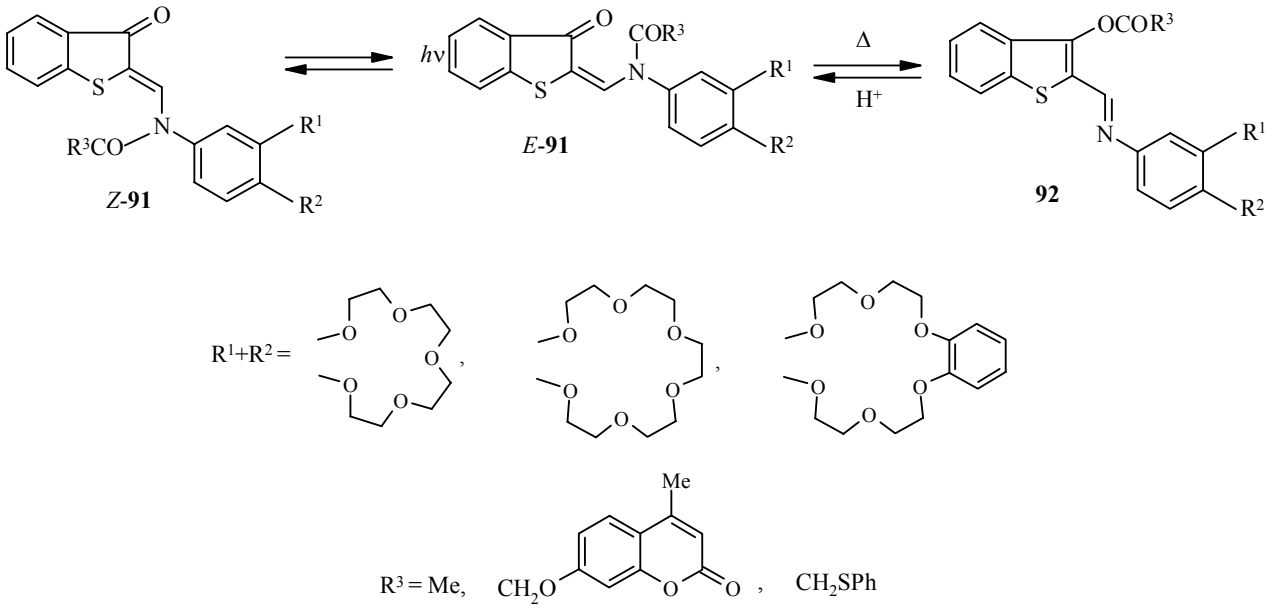
a $R^1+R^2=$  ; **b** $R^1+R^2=$  ; **c** $R^1=H$, $R^2=$  ;

d $R^1+R^2=$  ; **e** $R^1+R^2=$  ; **f** $R^1+R^2=$  ;

g $R^1+R^2=$  ;

88, **89** $R^3=(CH_2)_nSO_3^-$; *o*-$CH_2C_6H_4SO_3^-$; *p*-$CH_2C_6H_4SO_3^-$

The acylated crown-containing keto enamines of the benzo[*b*]thiophene series **91** that we synthesized are capable of switching on and switching off their sensor characteristics under the influence of light [129-131]. Irradiation of the compounds at the long-wave absorption maximum with light with λ_{irr} 436 nm leads to *Z*/*E*-isomerization at the C=C double bond followed by thermal N→O acyl transfer with the formation of the sensor-active O-acyl isomers **92** with high yields.



The reverse O→N migration of the acyl group can be realized catalytically.

The reaction of the O-acyl forms **92** with the cations of alkali and alkaline-earth metals leads to significant changes in the electronic absorption spectra; there is an increase in the molar extinction coefficient, accompanied by a hypsochromic effect, while the largest changes are observed for the benzo-15-crown-5-ether derivatives in the case of Ca^{2+} ions and for (di)benzo-18-crown-6-containing derivatives in the case of Ba^{2+} ions.

Thus, the published data in this review demonstrate the significant advances that have been made in the development of chemosensors, where the most significant results were obtained in the last 10-15 years. Nevertheless, it is clear that the creation of new effective, selective, and synthetically accessible chemosensors for the cations of metals remains as before an urgent task.

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