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Fluorescent and photochromic chemosensors

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Abstract. Data on organic chemosensors published over recent years are surveyed and described systematically. The bibliography includes 165 references.

I. Introduction

The creation and development of highly sensitive and reliable methods for the quantitation of various elements and their compounds in the environment (atmosphere, hydrosphere and lithosphere) is of current interest in chemistry. Success in solving this task requires that scientific studies be carried out to find the most selective reactions of atoms, ions or molecules which make it possible to determine qualitative and quantitative parameters of an object under study. The search for a selective reaction implies that one needs to find the transformation of the object being studied from a series of other transformations, which converts the substrate into the most convenient form with specific physical characteristics.

Of the many methods used to analyse substrates based on their physical properties (atomic absorption spectroscopy, ion-selective pM-metry (where pM is the negative logarithm of the metal ion concentration), electron microprobe analysis, neutron activation analysis, *etc.*), a special place belongs to electron spectroscopic methods,[1] fluorescence analysis being the most sensitive of these methods.[2]

An organic analytical reagent employed in fluorescence analysis should have a receptor which reacts selectively with the substrate, a signal-generating fragment and a conductor (bridge) between these parts of the molecule.[3] Such a system is called a chemosensor. If a fluorophore is the signal-generating part of a chemosensor, then this is a fluorescent chemosensor. Interaction of the receptor with the substrate followed by transfer of the energy of this interaction through the bridge to the fluorophore changes the spectral signal of the fluorophore, which allows one to make conclusions about the nature of the substrate. It became obvious while developing chemosensors that the set of fluorophores is rather limited, whereas the types of receptor are rather diverse. The most common chemosensors are represented by ionofluorophores; of these, reagents for various cations are used most widely.

Figure 1 shows a schematic diagram of the operating principle of chemosensor for cations.[4] The receptor of such a chemosensor is an electron donor (D), whereas the fluorophore is an electron acceptor.[5, 6]

Excitation of the fluorophore results in electron transfer from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). This enables electron transfer from the HOMO of the donor (receptor) to the HOMO of the acceptor (fluorophore), thus quenching the fluorescence of the latter. This phenomenon is known as the PET (Photoinduced Electron Transfer).[7] Once a cation (shown as a ball in Fig. 1) has been attached to the receptor, the HOMO energy level of the latter becomes lower than that of the fluorophore, the PET is no longer possible, and the sensor starts to fluoresce.

The majority of fluorescent sensors fit this scheme. However, a different PET mechanism is possible in the case of transition metal cations. In this case, the electron transfer is directed from the fluorophore to the bound metal ion.[8]

If the fluorophore of the sensor incorporates an electron-donor fragment in addition to the electron-withdrawing one, then the so-called PCT mechanism (Photoinduced Charge Transfer) is also observed due to the interaction between the similarly or oppositely charged poles of the fluorophore and the receptor. This effect is observed as a bathochromic or hypsochromic shift of

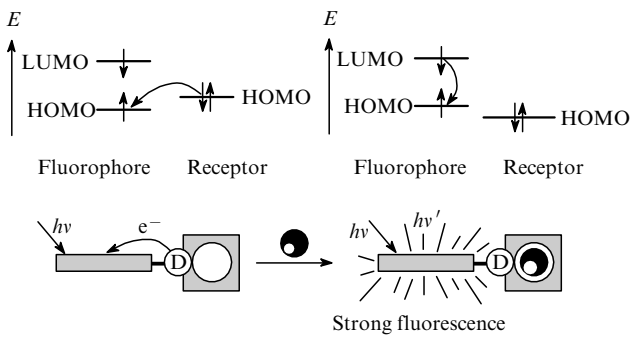


Figure 1. Schematic diagram of cation recognition fluorescent PET sensor.[4]

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absorption and emission bands in the spectra, and also as changes in the extinction parameters.[4]

Fluorescence of sensors may get enhanced or quenched if exciplexes † or excimers ‡ appear due to the formation of complexes between the receptor and the substrate.[4]

Fluorescent sensors have certain advantages over other optical chemosensors. The fluorescence method is very sensitive (in certain cases, a few molecules of an object can be detected). These experiments are inexpensive and easy to perform; the method has high resolving power in the wavelength and time measurement scales. Furthermore, luminescence spectra are quite sensitive to both structural changes in the sensor and substrate molecules and the external conditions.[6, 9–12]

Thus, the fluorescence method makes it possible to both solve purely analytical problems and control chemosensor processes.

When Fabbrizzi and Poggi [10] introduced the concept of 'switchable sensors', they distinguished such systems that can be triggered or blocked by changing the pH or the concentration of metal ions in the environment, by applying an external redox potential, *etc*.

The original photo-switching method is based on the photochromism phenomenon. If the sensor is associated with one state of a bistable photochromic device, the sensor function can be reversibly switched on or off by means of a photoreaction.

In this review, recent achievements in the development of organic chemosensor systems are classified and generalised. Fluorescent sensors are considered in the most detail.

II. Fluorescent cation sensors

According to a classification by de Silva,[11, 13] fluorescent cation sensors can be subdivided into four types.

1. Organic molecules that emit light due to the presence of a metal ion.

2. Organometallic complexes containing a metal which emits light.

3. Organometallic complexes which emit light due to interaction with a different metal ion.

4. A complex of two organic compounds which emits light in the presence of an organic 'guest'.

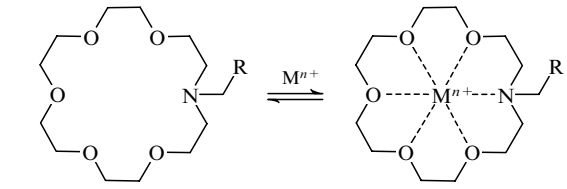
Although this classification of sensors is quite versatile, the need arose recently to expand it and make it more specific, because many new publications have appeared in the field of chemosensors. Detailed reviews have been published in which chemosensors were classified according to the type of interaction between the coordinating, luminescent and conducting parts of the system,[14, 15] as well as reviews dealing with the fundamentals of designing ionofluorophores for general analysis of cations,[4] transition metal ions,[16] anionic substrates,[17, 18] *etc*.

In this review, we have tried to emphasise the role of the receptor as the most functional part of a chemosensor molecule and to show the sensor capacities of various reactive series of compounds containing the same molecular receptors.

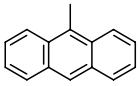
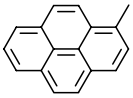
1. Azacrown ethers

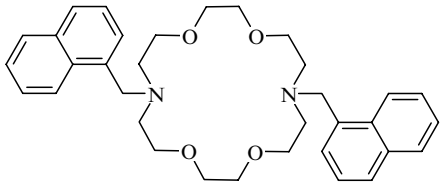
Chemosensors in which crown ethers serve as receptors belong to the most popular type of cation sensors of various metals. In order to enhance the efficiency of the crown ether receptor, the macrocycle is usually modified by incorporating nitrogen atoms, which are potent complexation centres.

Compound **1a** is the simplest azacrown-containing PET sensor.[19]



1a–c

R =  (**a**),  (**b**),  (**c**).



2

For example, if compound **1a** coordinates the K^+ ion, its fluorescence quantum yield in methanolic solutions increases from 0.003 to 0.14. Incorporation of several (more than three) methylene units between the nitrogen atom of the azacrown ether and the aromatic substituent, *i.e*., between the receptor and the fluorophore, results in an abrupt decrease in the PET.[20]

Aza(diaza)-18-crown-6 ethers bound to fluorophores (polynuclear aromatic hydrocarbons) through an *N*-methylene bridge (**1b**,**c** and **2**) were used in order to discriminate between mono- and divalent metal ions.[15, 21] The nature of the solvent and the type of anion in the salt being analysed may affect considerably the character of coordination, and hence the strength of the PET.[22, 23]

The interaction of the sensor **1c** with thiocyanates of mono- and divalent metals can serve as an example; the spectral pattern of this interaction is shown in Fig. 2.[15] Divalent and ammonium cations display the standard PET with luminescence enhancement. Conversely, coordination of monovalent cations results in luminescence quenching. This anomaly can be rationalised by the existence of specific coordination of monovalent cations with the

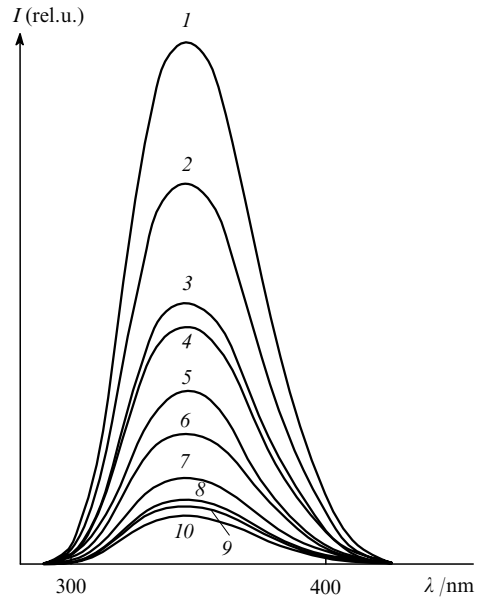


Figure 2. Fluorescence spectra of compound **1c** and its complexes with various metal ions in methanol;[15]
(*1*) Ba^{2+} complex; (*2*) Ca^{2+} complex; (*3*) Zn^{2+} complex; (*4*) NH_4^+ complex; (*5*) Mg^{2+} complex; (*6*) compound **1c**; (*7*) Li^+ complex; (*8*) Na^+ complex; (*9*) Cs^+ or Rb^+ complex; (*10*) K^+ complex.

† An exciplex is an excited molecular complex. It is formed upon association of two molecules (which may be similar or different), one of which is in the ground state while the other is in an excited state.

‡ An excimer (a specific case of an exciplex) is an excited dimer formed from two similar molecules, one of which is in an excited state while the other one is in the ground state.

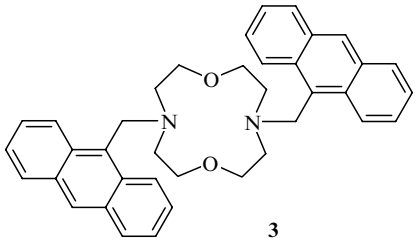
azacrown ether and the thiocyanate anion, providing additional transfer of electron density from the anion to the naphthalene chromophore.[15]

Using electronic spectra, ^1H and ^{13}C NMR spectra and X-ray diffraction analysis, it was shown that the PET affects the physical characteristics of complexation for a number of sensor series. For example, enhancement of fluorescence in the presence of various 'guest' cations occurs in derivatives of diazacrown ethers containing two, three, or four oxygen atoms in the ring and two fluorescent substituents. There are two reasons that can explain this phenomenon.

1. Quenching of fluorescence in the chemosensor molecules due to intramolecular electron transfer between the fluorescent 'pendants' and two nitrogen atoms of the ring. As a result, coordination of a cation by the crown ether enhances light emission.

2. Coincidence between the steric parameters of the receptor and the substrate and a suitable rate of cation exchange between the free ligand and the complex in the ground state.

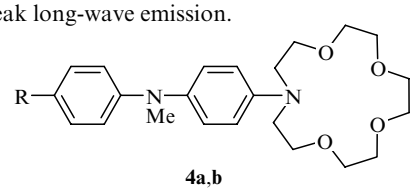
It was found[15] that Zn^{2+} ions are coordinated to both nitrogen atoms of the ring, which results in enhancement of luminescence of diaza-12-crown-4 ether **3** by a factor of 182.



3

It was shown[15] that diaza-18-crown-6, which has two 1-pyrenyl substituents, can be used as a fluorescent sensor for alkali metal ions.

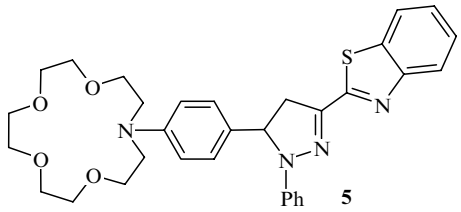
Ionofluorophores **4a**,**b** are suitable for the quantitative determination of Ca^{2+} ions in solutions based on changes in luminescence spectra upon complexation,[24] but they behave differently. For example, the $Ca^{2+} \cdot$ **4a** complex displays an intense fluorescence band, unlike the $Ca^{2+} \cdot$ **4b** complex which is characterised by weak long-wave emission.



4a,**b**

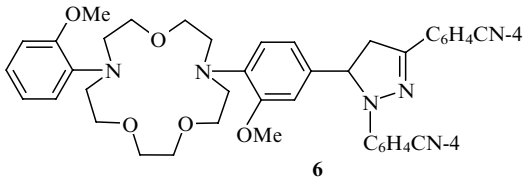
R = H (**a**), NMe_2 (**b**).

The *N*-aryl receptor of the azacrown sensor **5** with decreased basicity of the nitrogen atom of the crown macrocycle is characterised by strong luminescence enhancement (by a factor of 28) upon interaction with the Ca^{2+} ion in acetonitrile,[25] the fluorescence life time being increased from 0.28 to 3.6 ns.



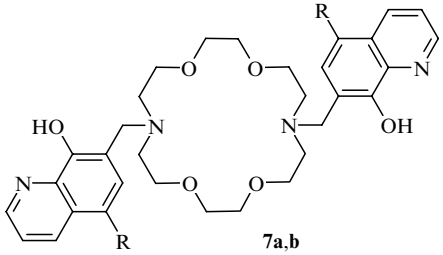
5

The coordination sphere of crown ethers can be expanded by introducing substituents containing additional donors. For example, the sensor **6** is a good fluorescent reagent for 'softer' sodium ions[13] due to involvement of the electron pairs of the *o*-methoxy groups in coordination.



6

Additional coordination sites are also present in compound **7a**, which is a highly selective luminescent sensor for magnesium ions effective in solutions with pH > 6.[26]

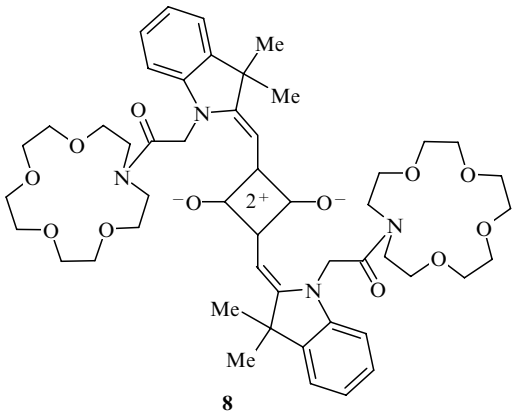


7a,**b**

R = Cl (**a**), NO_2 (**b**).

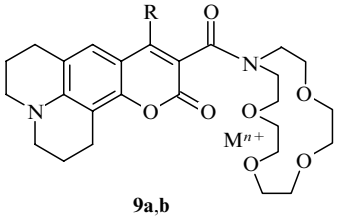
An analogous ion-selective chemosensor ligand **7b** has high sensitivity and affinity for Hg^{2+} ions over a wide range of pH.[27]

Yet another way to enhance the efficiency of sensors is to incorporate zwitter-ionic fragments. For example, excess electron density on the oxygen atoms of the central zwitter-ionic fragment in the luminescent sensor **8** makes it highly efficient with respect to lithium ions in acetonitrile – dichloromethane system.[28]



8

Similarly, the efficiency of chemosensors **9a**,**b** for divalent metal ions (Ca^{2+}, Mg^{2+}, Ni^{2+}, Zn^{2+}, Cu^{2+}) can be explained by the presence of a quinolizine and coumarin nuclei in the fluorophore.[29, 30] It was shown[30] that charge transfer from the nitrogen atom of the quinolizine part of the molecule to the carbonyl group of the coumarin part occurs in compounds **9a**,**b**. A strong PCT effect is realised in these molecules, and the electronic spectra manifest bathochromic shifts.[30]

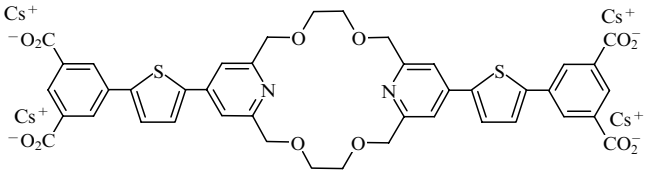


9a,**b**

R = H (**a**), CF_3 (**b**).

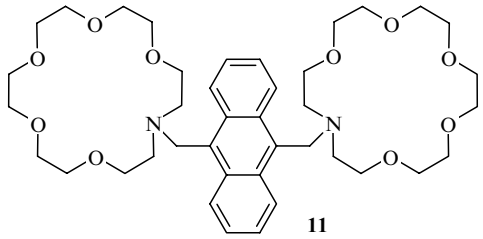
Yet another approach to specific chemosensors is the introduction of extra functional groups into the known sensors resulting in alteration of their properties. For example, introduction of carboxyl-containing thiophene derivatives as fluorophores into dipyridino-crown ether makes the resulting caesium tetracarboxylate **10** water-soluble, which is very important for practical use. The fluorescent sensor itself has high selectivity for potassium

ions, because the bulky caesium cations do not compete with potassium ions in solution for the coordination by the cavity of this dipyridinocrown ether.[31]



10

Modification of compound **1a** by addition of one more azacrown fragment results in the sensor **11** which can recognise dications. For example, ammonium groups located at α- and ω-carbon atoms of the substrate alkane chains enhance considerably the fluorescence of the sensor **11**; they are probably incorporated into both fragments of the crown ether.[32]

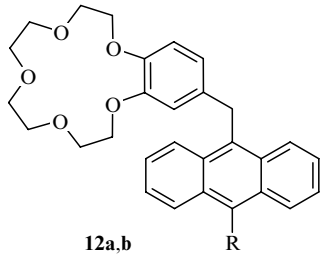


11

Azacrown ethers are characterised by rather a high basicity of the nitrogen atoms. On the one hand, the high basicity of the nitrogen atom increases the chemosensor efficiency and provides a stable PET; on the other hand, undesirable protonation occurs in acidic solutions. Crown-ether ligands are devoid of this drawback.

2. Crown ethers

Benzocrown ether **12a** was one of the first to be suggested as PET sodium ion sensor. When this compound is coordinated by the sodium cation in suitable solvents, fluorescence is enhanced.[33, 34]



12a,**b** R

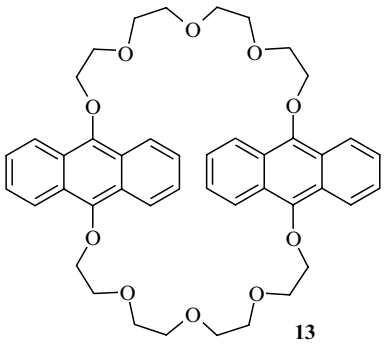
R = CN (**a**), CH_2N O (**b**).

Compound **12b** is a so-called 'switchable' fluorescent sensor which operates in acidic media, where the electron-donating morpholine substituent is protonated in the first stage.[35]

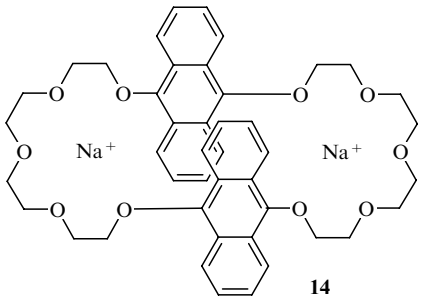
Other fluorescent indicators for the Na^+ and K^+ ions based on benzocrown ethers have been synthesised and studied (see Ref. 36).

1,8-Anthraceno-18-crown-5 is a luminescent sensor for ions of alkali and alkaline-earth metals.[37] Fluorometric titration was used to determine the stability constants of its complexes and their dependences on the cation parameters.

Bis(anthracene-9,10-diyl)coronand **13** is a sensor for Na^+ and K^+ ions. It was shown[38, 39] that gradual addition of sodium perchlorate to solutions of compound **13** in methanol or acetonitrile gives a stable excimer complex **14** with the composition 1 : 2, which is the reason for enhancement of the corresponding luminescence. K^+ ions form a 1 : 1 complex.

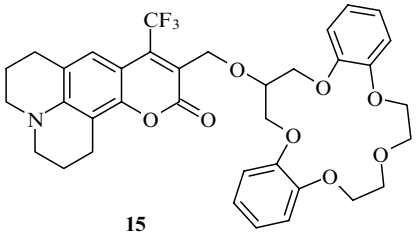


13



14

Combination of the coumarin fluorophore with benzocrown receptors results in efficient chemosensors. For example, strong substituent polarisation in sensor **15** in an excited state results in additional coordination of alkali and alkaline-earth metal ions with the carbonyl group of the coumarin fragment.



15

This effect is observed in luminescence spectra as a bathochromic shift of the bands (Fig. 3);[4] the strongest quenching is observed in the presence of the Ca^{2+} ion. The selectivity of Ca^{2+}

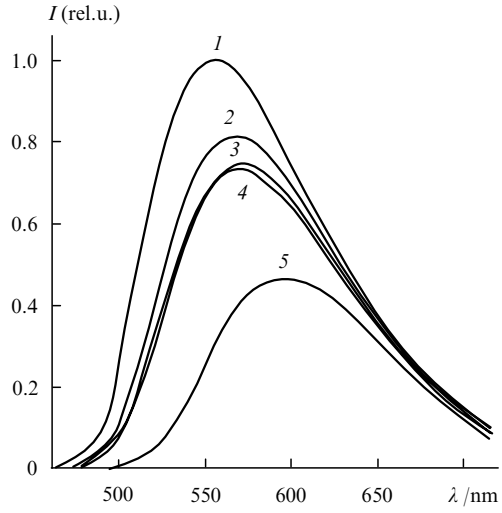
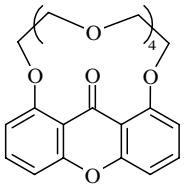


Figure 3. Fluorescence spectra of compound **15** and its complexes with metal ions in acetonitrile;[4]
(*1*) the ligand; (*2*) K^+ complex; (*3*) Na^+ complex; (*4*) Li^+ complex; (*5*) Ca^{2+} complex.

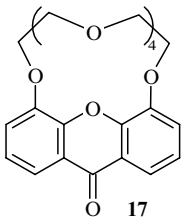
sensor **15** is very high: the ratio of stability constants of the complexes is $k(Ca^{2+}):k(Mg^{2+}) = 12\,500$; $k(Na^{+}):k(K^{+}) = 16$.

A few other sensors containing the coumarin fragment are known. For example, 4-substituted benzo-α-pyronebenzo-12-crown-4, -15-crown-5, and -18-crown-6 in acetonitrile are luminescent sensors for Li^{+}, Na^{+}, K^{+}, and Mg^{2+} ions (see Refs 40 and 41). The effect of the macrocycle size on the extent of fluorescence quenching during the formation of 1 : 1 complexes was studied.[42]

The crown ethers **16** and **17** containing the dihydroxyxanthone fragment have different properties: compound **16** has high affinity for barium ions, whereas the cavity in compound **17** binds selectively potassium ions. In the former case, luminescence is enhanced as the ion concentration increases; in the latter case, it is quenched.[43]

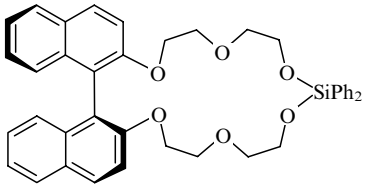


16

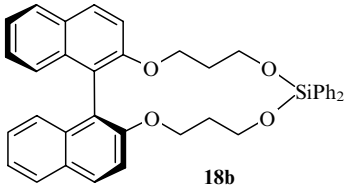


17

Unusual fluorescent sensors, namely, optically active silacrown ethers **18a**,**b** were synthesised.[44] Compound **18a** is a selective reagent for lithium ions and viologen bromide, while compound **18b** reacts with the latter to give rotaxane-like structures.

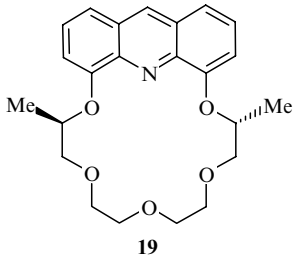


18a



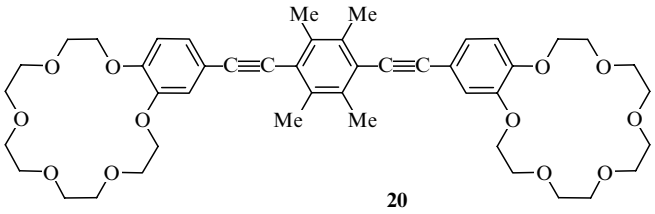
18b

The enantiomerically pure chiral ligand, *viz*., acridinodimethyl-18-crown-6 (**19**), displays high enantioselectivity and gives luminescent complexes with chiral ammonium ions in acetonitrile.[45] The authors of this study give well-reasoned evidence that it is possible to design a series of efficient enantioselective chemosensors for chiral substrates.

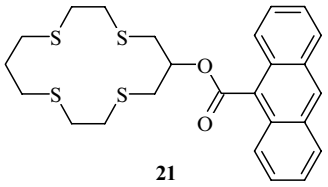


19

Xia *et al.*[46] described the synthesis of the luminescent sensor **20** containing 1,4-di(phenylethynyl)tetramethylbenzene as the chromophore and 18-crown-6 as receptors and discussed its photochemical properties. The chromophore luminescence is considerably quenched only by those lanthanide ions which have large ionic radii and in which *f*–*f* transitions occur (Ce^{3+}, Pr^{3+}, Nd^{3+}). Ions of alkali and alkaline-earth metals, as well as lanthanide ions with smaller radii, do not greatly affect the emission spectra of this sensor.



20



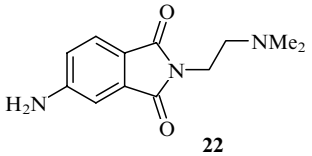
21

Thiacrown ether **21** is selective for Cu^{2+} ions. It is interesting that a 'reverse' PET operates in this complex, and fluorescence quenching occurs due to electron density shift from the anthracene substituent to the copper cation possessing strong oxidising properties.[47]

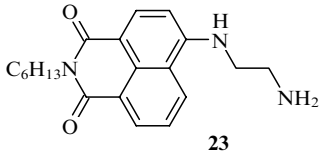
Thus, depending on the ring size and configuration, crown ethers may be selective for ions of alkali, alkaline-earth, or rare-earth metals.

3. Sensors with polyamine receptors

Even compound **22**, which is a rather simple diamino derivative, can form complexes with Cr^{3+}, Fe^{3+}, Co^{2+}, Ni^{2+}, and Cu^{2+} ions; it manifests the PET and acts as a chemosensor with 30-fold fluorescence enhancement.[48] The sensor **23** acts in a similar way but with higher selectivity for copper ions.[49]

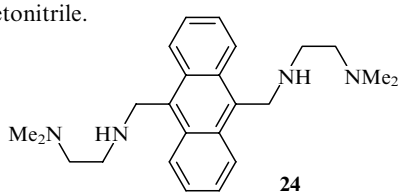


22



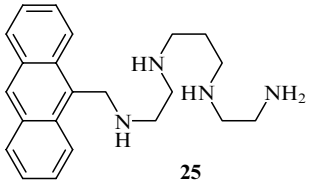
23

The anthracene derivative **24** was the first example of a chemosensor with a short polyalkylamine chain, which forms chelate complexes with transition metal ions.[50] The ligand fluorescence, which is very weak due to the PET process, becomes 1000 times more intense upon addition of zinc chloride in acetonitrile.



24

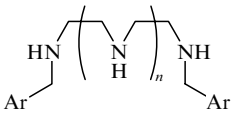
The action of chemosensors of the type **25** depends on the nature of the substrate cations and on the acidity of solutions. Coordination of Cu^{2+} and Ni^{2+} ions with compound **25** does not result in intense light emission in weakly acidic and neutral solutions (pH > 4) where the amino groups are not protonated and the PET operates. This results from deactivation of the excited state *via* the energy levels of the metal centre.



25

On the contrary, a complex of compound **25** with Zn^{2+} luminesces strongly due to the d^{10} configuration of the Zn^{2+} ion and an increase in the oxidation potential of amines.[51]

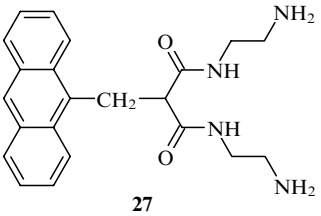
A large series of open-chain and cyclic *N*-mono- and *N*,*N*-diarylpolyalkylamines has been synthesised and analysed.[52] Compounds **26** are chemosensors for proton and transition metal ions: Co^{2+}, Ni^{2+}, Cd^{2+}, Pb^{2+}, Cu^{2+}, Zn^{2+}. Protonation or coordination of cations change the fluorescence accordingly. Sensors **26** where Ar are terminal anthracene substituents can form excimers.



26

$n = 0-4$.

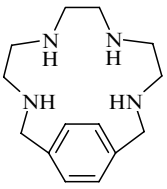
Ligands containing aminoethylamide fragments (*e.g.*, compound **27**) are effective in recognition of Ni^{2+} and Cu^{2+} cations. It is believed that photoexcitation involves electron transfer from the metal ions to the ligand.[53]



27

Fluorescent complexes with the composition ML_2^{2+} [where L is 6-(9-fluorenyl)-1,4,8,11-tetraazaundecane-5,7-dione and M is a divalent ion of copper, nickel or cobalt] were studied in non-aqueous and aqueous media.[54]

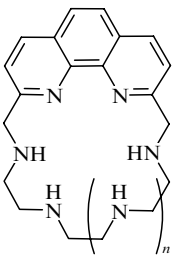
It was found that open-chain polyamines are more efficient sensors than cyclic polyazacyclophanes **28**.[52]



28

In a molecule of compound **28**, the polyamine chain is arranged as a strained arch above the benzene ring plane. As a result, simultaneous coordination of both benzyl nitrogen atoms by a single metal ion becomes impossible. However, the PET can still operate in the complex.

The situation changes if the ring size increases or if additional nucleophilic centers are introduced. For example, macrocyclic ligands **29a**,**b**, in which the receptor ring contains a 1,10-phenanthroline fragment, are chemosensors for hydrogen and zinc cations.[52]

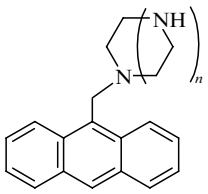


29a,**b**

$n = 1$ (**a**), 2 (**b**).

Compound **29a** forms only a mononuclear complex with zinc, whereas compound **29b** forms both mono- and binuclear complexes. Thus, fluorescence spectra depend on the degree of protonation and complexation.

Rather efficient chemosensors for Zn^{2+}, Cd^{2+}, and Hg^{2+} were obtained based on anthracene-substituted polyazacrown ethers **30** (see Ref. 55).

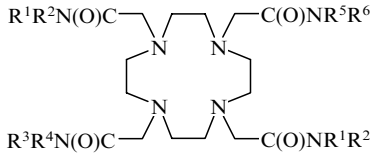


30a–**e**

$n = 1$ (**a**), 2 (**b**), 3 (**c**), 4 (**d**), 5 (**e**).

The luminescence of compounds **30c**,**e** is pH-dependent and increases abruptly upon complexation with Zn^{2+} or Cd^{2+} in water. On the contrary, Hg^{2+} ions quench the residual fluorescence of compounds **30a**–**e**.

The fluorescent properties of macrocyclic ligands **31a**–**d**, containing *N*-(β-naphthylmethyl)amide groups as fluorophores, were studied in water and acetonitrile. All ligands **31** display the typical fluorescence of the naphthalene chromophore (λ_{max} = 337 nm); however, it is weakened due to the PET. The emission spectra of compounds **31b**–**d** contain additional broad bands typical of the naphthalene excimer (λ_{max} = 397–401 nm). The ligands show different luminescent properties in the presence of quenching ions (Pb^{2+}, Ni^{2+}, Cu^{2+}, Eu^{3+}) and ions that cause luminescence enhancement (Zn^{2+}, Cd^{2+}).[56]



31a–**d**

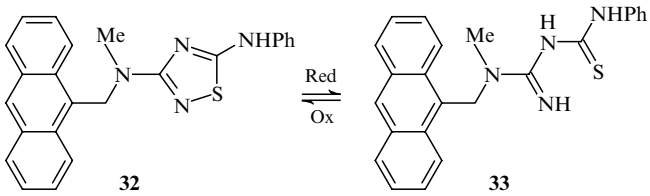
$R^1 = R^3 = R^5 = H$, $R^2 = R^4 = Me$, $R^6 = 2\text{-}CH_2C_{10}H_7$ (**a**);
$R^1 = R^3 = R^5 = H$, $R^2 = R^4 = R^6 = 2\text{-}CH_2C_{10}H_7$ (**b**);
$R^1 = R^3 = H$, $R^2 = R^4 = Me$, $R^5 = R^6 = 2\text{-}CH_2C_{10}H_7$ (**c**);
$R^1 = H$, $R^2 = Me$, $R^3 = R^4 = R^5 = R^6 = 2\text{-}CH_2C_{10}H_7$ (**d**).

When the ligand **31a** is coordinated with zinc or cadmium ions, the emission intensity increases by a factor of two; addition of Pb^{2+} salts quenches fluorescence by 25% (the heavy atom effect), while addition of Cu^{2+} quenches it by 95%. In the $Tb^{3+}\cdot$**31a** complex, fast deactivation processes predominate, which complicate spectroscopic studies. If Cd^{2+} ions are added, the intensity of the short-wave radiation of protonated sensor **31b** in acetonitrile increases, whereas the excimer band disappears quickly. Similarly, emission is quenched by Pb^{2+} ions. The reason for this is that naphthyl excimers cannot be formed in these complexes because of spatial hindrance. Complexation of the ligand **31c** with metal ions (Zn^{2+}, Cd^{2+}, Pb^{2+}, Ni^{2+}, Cu^{2+}, Eu^{3+}) occurs quickly even in aqueous solutions. Its behaviour in the presence of various ions resembles that of compound **31a**. Coordination of compound **31d** (which is more strained spatially) with metal ions is hindered. The Zn^{2+} and Cd^{2+} ions affect very weakly both the total intensity of fluorescence of the ligand **31d** and the ratio of emission from the monomer and excimer. On the other hand, the Pb^{2+}, Ni^{2+} and Cu^{2+} ions decrease the total emission (by 36%, 37% and 86%, respectively) by affecting considerably the excimer band.

Various physical methods were used to study whether it is possible to determine copper, nickel, zinc, cadmium, mercury, and lead cations using a series of polyaza- and oxazacycloalkanes (14 to 18 units) containing peripheral anthrylmethyl fluorophores. It was found that all metals studied form stable complexes with these ligands in dioxane–water and THF–water media.[57] Copper(II) ions selectively quench the fluorescence of sensors in neutral and acid media; the intensity of luminescence of the 1,4,10-trioxa-7,13-

diazacyclopentadecane ligand increases selectively in the presence of mercury(II) ions in basic medium.

Novel fluorescent chemosensors **32** and **33** for heavy metal ions were suggested.[58] Since the reduced form **33** is readily transformed into the oxidised form **32**, these compounds may be considered as two components of a switchable redox system.



32 **33**

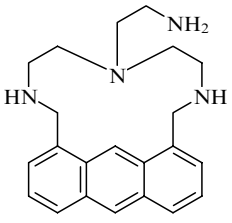
The oxidised form **32** binds mercury ions with a 44-fold increase in fluorescence; the carbamimidoylthiourea fragment of molecule **33** interacts with cadmium ions with a six-fold increase in the fluorescence intensity.

In the majority of fluorescent chemosensors considered above, which incorporate monocyclic or open-chain receptors containing nucleophilic atoms such as O, N, and S, the structures and electronic properties are affected by substrates (in most cases, cations). Nitrogen-containing podands and rings have sensor properties only with respect to hydrogen and transition metal ions. Incorporation of oxygen receptor atoms makes it possible to expand the range of cations that can be analysed (alkali and alkaline-earth metals; rare-earth elements; ammonium ions) and to improve selectivity. The selectivity and sensitivity of chemosensors increase upon transition from two-dimensional molecules to three-dimensional systems that coordinate substrate species in a 'host – guest' fashion in molecular cavities of specific sizes.

4. Tetraaminoalkyl three-dimensional sensors

Some planar chemosensors contain functional substituents which fix a cation or some other substrate outside the plane. As an example, the molecules **6** – **9a**,**b**, **15**, and **31a** – **d** have additional complexation sites located outside the main coordination plane. A tertiary nitrogen atom in a pyramidal configuration often serves as a vertex of a complex molecular frame forming a cavity.

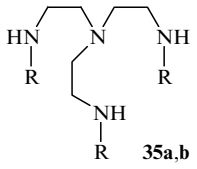
For example, compound **34** containing four nitrogen atoms is a selective sensor for Cu^{2+} and Hg^{2+}. In neutral media, its fluorescence is quenched due to formation of chelates with copper (18-fold) or mercury cations (fourfold).[59]



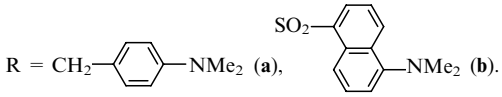
34

The sensor **35a** containing *p*-*N*,*N*-dimethylaminobenzyl fluorophores has an emission band at $\lambda = 360$ nm.[60] The fluorescence of sensor **35a** in solution in the presence of Cu^{2+} ions reaches a maximum at pH 3.8 (protonated form); as the pH is increased and protons are replaced by copper ions, fluorescence is progressively quenched and disappears at pH 5.5. Thus, the system **35a** – Cu^{2+} is an efficient switchable pH-dependent sensor.

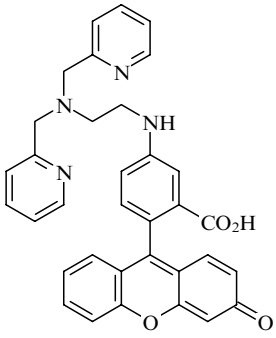
The fluorescence of compound **35b**, which contains 5-dimethylaminonaphthalenesulfonyl (dansyl) substituents as chromophores, does not depend on the pH of the medium in the range from 3 to 11. However, complexation with such ions as Cu^{2+}, Co^{2+}, Zn^{2+}, and Cd^{2+} at pH 9.5 affects strongly the luminescence: Cu^{2+} and Co^{2+} quench luminescence, whereas Zn^{2+} and Cd^{2+} enhance it. At pH 6, only Cu^{2+} ions form a complex, which makes compound **35b** a highly selective sensor for copper ions under physiological conditions.[61]



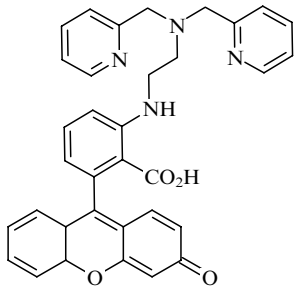
35a,**b**



In certain sensors, some of the nitrogen atoms may be involved in heterocycles; for example, this is the case for the sensor **36a** which has high selectivity for zinc ions and may be used to analyse biological objects. Its isomer **36b**, in which the polyamine substituent is at position 6 of the benzene ring, is also highly selective for Zn^{2+} ions. The fluorescence of original starting compounds is almost independent of the medium acidity; it is virtually absent at pH 7.5. However, the fluorescence of compound **36a** becomes 17 times more intense as zinc ions are added, whereas that of the 6-substituted isomer **36b** becomes 51 times more intense.[62]

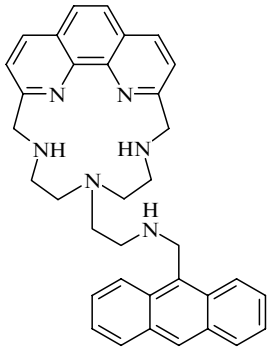


36a



36b

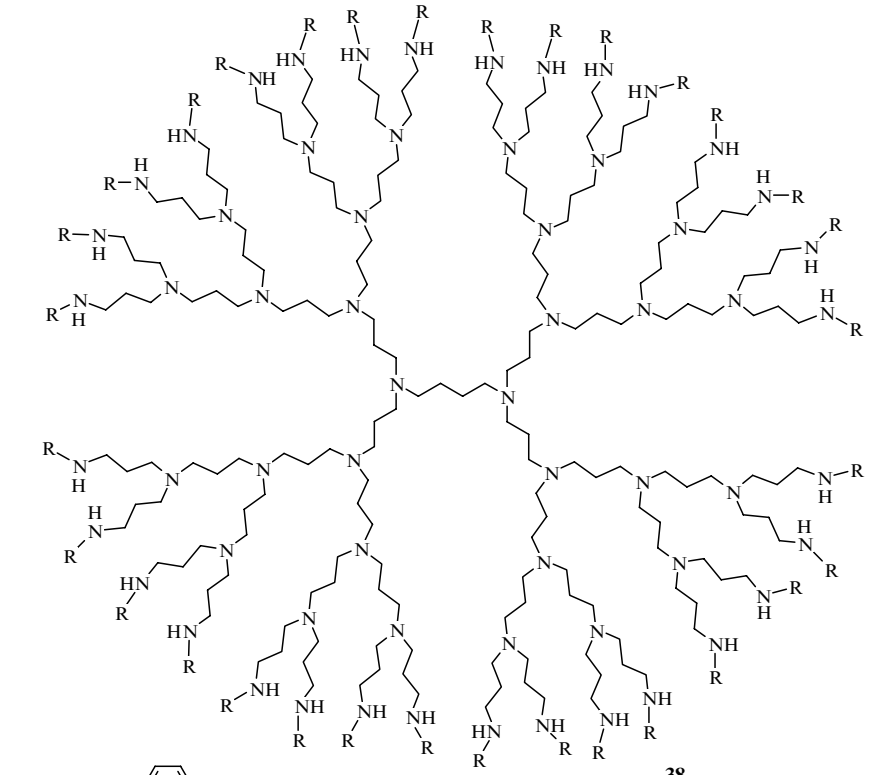
The fluorescence of the sensor **37** is quenched owing to the PET. At appropriate pH values and concentrations of the coordinating Zn^{2+} ions, reversible formation (decomposition) of the exciplex occur because the phenanthroline and anthracene parts of the molecule become closer (or farther, respectively). This allowed Bencini *et al.*[63] to classify this system as a 'molecular machine' controlled by pH and light.



37

Balzani *et al.*[64, 65] used polymeric compositions (dendrimers) based on polypropyleneamine with dansyl end groups (*e.g.*, compound **38**) as luminescent Co^{2+} sensors.

The amine fragments create a polycellular internal cavity which coordinates the cations. The formation of the complex with the Co^{2+} ions does not affect the absorption spectra, but it strongly quenches the radiation from the peripheral fluorophores; one cell of the dendrimer reversibly coordinates one cation. Zinc ions do not affect the properties of dendrimers; in the presence of Cu^{2+} cations, the macromolecule undergoes irreversible changes.

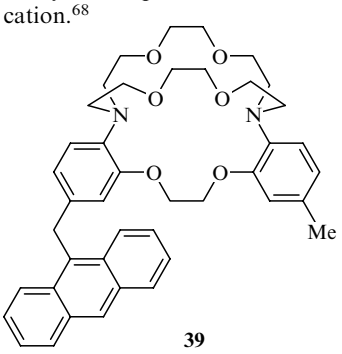


38

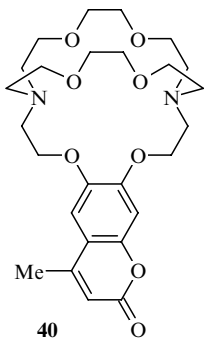
R = —SO_2— NMe_2

5. Cryptands

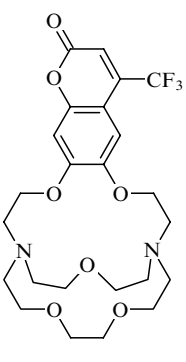
Attachment of an out-of-plane bridge to azacrown ethers results in cryptands, which represent sensors with enhanced receptor capacity.[66] For example, the PET is observed in the molecules of cryptands **39**–**41**. The cavity size in these compounds governs the selectivity: the parameters of the receptors in compounds **39** and **40** match the diameter of the K^+ ion (see Ref. 67), whereas the cavity in compound **41** is suitable for coordinating the sodium cation.[68]



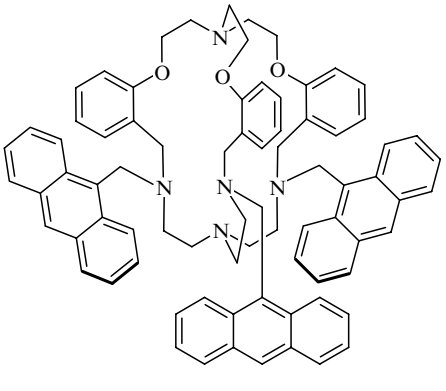
39



40



41



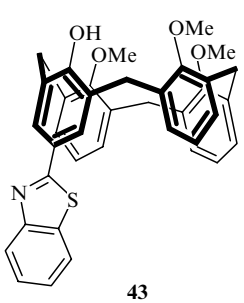
42

In order to determine transition metal ions, it was suggested to use cryptand sensors of the type **42**, which form 1 : 1 adducts with Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Pb^{2+} cations in THF with an accompanying strong increase in the sensor fluorescence.[69] Of these cations, the strongest effect is observed in the case of Zn^{2+}. Silver and mercury ions, which have larger ionic radii, cannot form complexes. The properties of compounds **40**–**42** are strongly pH-affected.[4, 70]

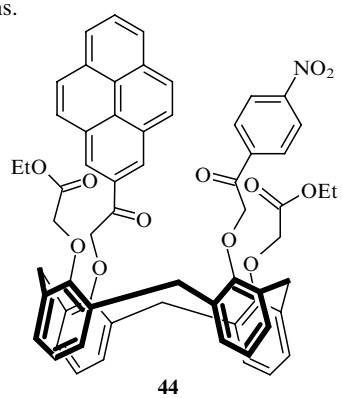
6. Calixarenes

Various calixarene and -hetarene derivatives can also be used as efficient sensor systems. Spatially hindered calixarenes are not very good ligands to form stable complexes; however, they can serve as a supramolecular base for adding diverse receptors and fluorophores. This results in sensors containing cavities with different sizes and properties suitable for several types of 'guest' species.

One of the first simple calix[4]arene systems **43** containing a benzothiazole fluorophore showed selective properties as a sensor for lithium ions.[71] The Li^+ cations replace the phenol proton and coordinate the methoxy groups, thus causing a bathochromic PCT-shift of the fluorescence band. This system shows no response to Na^+ and K^+ ions.



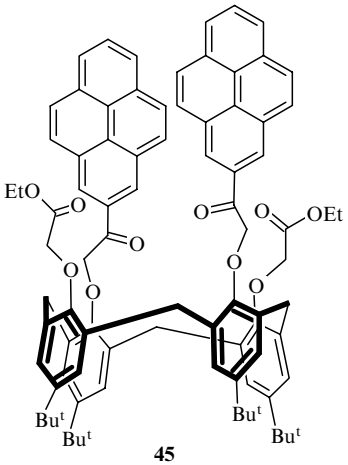
43



44

The cavity of yet another calix[4]arene sensor **44**, which incorporates ester groups, matches the size of Na^+ (see Ref. 72). Coordination with Na^+ breaks the spatial contact between the pyrene and nitrophenyl rings, which results in disappearance of the PET and enhances fluorescence by a factor of six.

Calixarene **45** is also suitable for the identification of Na^+ (see Ref. 73). Incorporation of the cation into the inner sphere of the sensor prevents the formation of an excimer from the pyrene units; as a result, only the monomer fluorescence remains in the spectrum of the complex. The selectivity factor [the ratio $k(Na^+):k(K^+)$] is 154; the presence of lithium cations does not disturb the system.



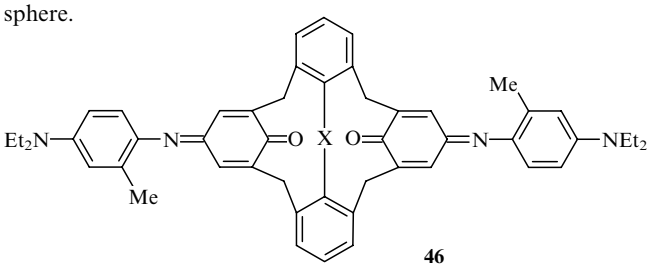
45

Ionophore **45** has recently been modified [74] by introducing a 9-anthroyloxyphenyl fluorophore into the molecule.

The electronic interactions in a series of calix[4]arene crown ethers and their complexes with alkali metal ions were studied. Absorption and emission electron spectroscopies have been used to reveal the effects of π-binding between the cations and the ligand; it was assumed that they have a major effect on the luminescent properties of the fluorophore.[75]

Many calixarene sensors contain crown ether fragments as receptors.

For example, calix[4]crown ether **46** is a strong ionochromophore.[76] If Ca^{2+} ions are added, they enter the cavities and interact with the electrons of the imino, keto, and crown-ether groups; a bathochromic shift occurs, which changes the colour of the compound from blue to green ($\Delta\lambda$ = 112 nm). This phenomenon is not observed in the presence of potassium ions; if the latter are coordinated with compound **46**, the spectrum of the latter is restored due to displacement of calcium ions from the inner sphere.



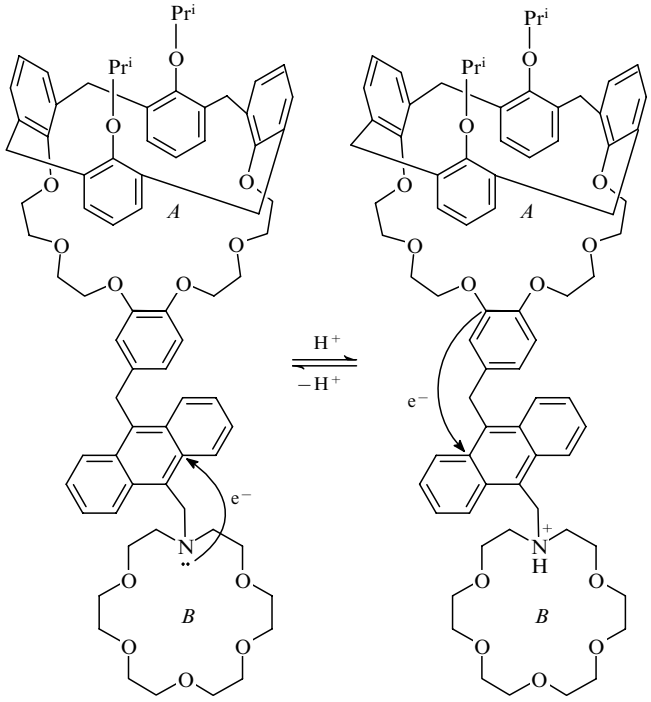
46

X = $OCH_2(CH_2OCH_2)_3CH_2O$.

Alkali metal cations affect strongly the excitation spectra of other calix[4]crown ethers containing two peripheral acetamidoanthraquinone residues.[77]

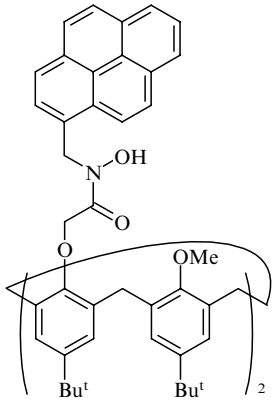
1,3-Alternating calix[4](9-cyano-10-anthrylmethyl)benzocrown-6 and its dideoxygenated analogue showed high selectivity towards the caesium ion when it was determined in the presence of a tenfold excess of potassium and rubidium cations.[78]

A more complicated calix[4]arene system **47** containing two crown receptors was suggested as an integrated sensor for the determination of potassium cations in alkaline medium and caesium cations in acidic medium.[79] The PET in alkaline solutions results in a very weak residual fluorescence of the anthracene fluorophore. Addition of caesium ions, which are coordinated by the cavity *A*, does not change the spectral characteristics. On the contrary, K^+ cations are incorporated into the cavity *B* of the crown ether, quench the PET and cause a sevenfold increase in fluorescence. In acidic media, where the nitrogen atom of the ring *B* is protonated, the PET is supported by the crown ether fragment *A*, and the fluorescence intensity is low. In this case, the ring *B* cannot coordinate potassium cations. Addition of Cs^+ ions to the solution results in their coordination by the ring *A* and a fourfold increase in fluorophore emission. Li^+ and Na^+ ions do not compete with each other in these processes, but rubidium cations display an effect resembling that of potassium cations in alkaline medium and that of caesium cations in acidic media.



47a **47b**

The range of cations that can be determined by sensors based on calixarenes is rather wide. Such sensors are suitable for analysis of not only alkali but also transition metal cations. For example, the bispyrenyl calix[4]arene **48** with two hydroxamic acid linkers is a good Cu^{2+} and Ni^{2+} sensors (see Ref. 80).

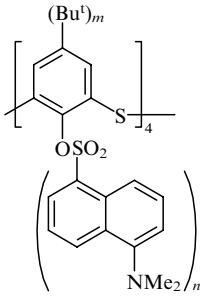


48

In solutions, compound **48** generates a double fluorescence spectrum, which corresponds to the monomeric and excimeric states of the pyrene rings. Addition of copper or nickel salts to the solution quenches abruptly a part of the fluorescent irradiation

depending on the solution acidity. In the opinion of Bodenant *et al.*,[80] the excimer photosensitivity of the ligand makes it possible to consider this system as a new type of chemosensor for the selective determination of transition metal ions in aqueous media.

The selectivity of sensors based on calixarenes may be enhanced by replacing the oxygen atoms in the calixarene skeleton by sulfur atoms. For example, water-soluble thiacalix[4]arenes **49** modified by dansyl fragments were suggested for the first time as fluorescent chemosensors for Co^{2+}, Ni^{2+}, and Cd^{2+}.[81]



49

$m = 0-4$; $n = 2-4$.

tert-Butyl groups decrease the sensitivity of sensor molecules. The thiacalixarene **49** containing one *tert*-butyl group ($m = 1$) and three dansyl residues ($n = 3$) was found to be the most efficient. The complexation constants of this compound with Co^{2+} and Cd^{2+} are 2380 and 1510, respectively. For comparison, the corresponding constants for the chemosensor **49** containing four *tert*-butyl groups ($m = 4$) and three dansyl residues ($n = 3$) are 130 and 250.

Calix[4]arene systems can be luminescent chemosensors for medium-radius lanthanides.

The recently obtained macrocyclic water-soluble tetra-*p*-sulfonylmethylcalixresorcin[4]arenes coordinated with Nb^{3+} or Eu^{3+} ions show a triplet transition with an analytical frequency of 24 400 cm^{-1} (see Ref. 82). In acetonitrile, the same ions form highly luminescent complexes with calix[4]arene crown ethers containing a 2,2′-bipyridine fragment.[83]

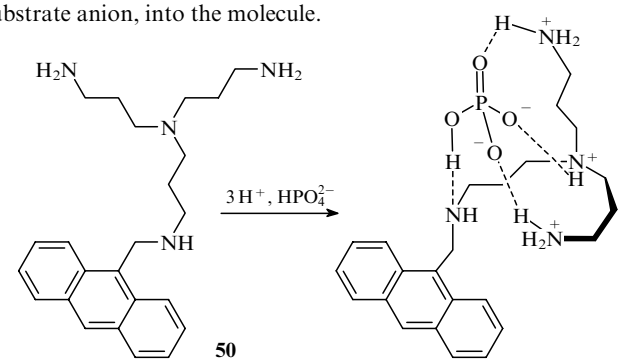
III. Fluorescent chemosensors for anions

The main types of sensor used for the determination of anions have been considered in detail in reviews [17, 18] and in a monograph,[84] hence here it is appropriate to dwell on the general principles for constructing such chemosensors and to discuss recent publications.

Design of luminescent sensors for anions is a more complex task than that for cations, for the following reasons.

1. Anions are usually larger than cations, hence the receptor should have a larger coordination space; in addition, because of a low charge density on the anion, the receptor should form rather strong bonds with the anion (at the hydrogen bond level).

2. Receptors for anions are commonly constructed on the basis of cation receptors by incorporating strong electrophiles (protons, metal cations) enabling reversible coordination of the substrate anion, into the molecule.

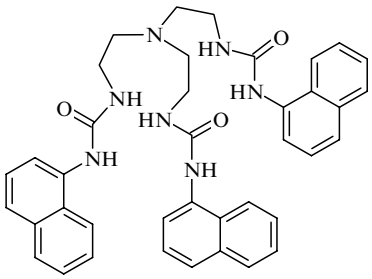


50

The system **50** was the first example of a fluorescent molecular sensor for anions.[85]

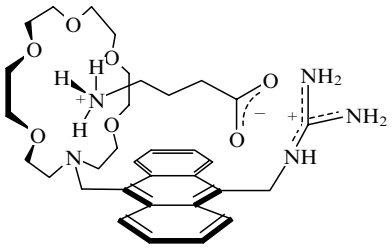
In aqueous solutions at pH 6, only three nitrogen atoms are protonated (the nitrogen atom closest to the anthracene fragment remains non-protonated), therefore the PET is effective and emission of the anthracene ring is small. If an HPO_4^{2-} anion is coordinated, the fourth H—N bond appears and fluorescence is enhanced.

Such anions as $H_2PO_4^-$ and HSO_4^- can be detected using the fluorescent system **51**, which incorporates three naphthylurea residues. The sensor **51** forms a 1 : 1 complex with $H_2PO_4^-$ in which the ligand fluorescence is enhanced owing to the PET.[86]



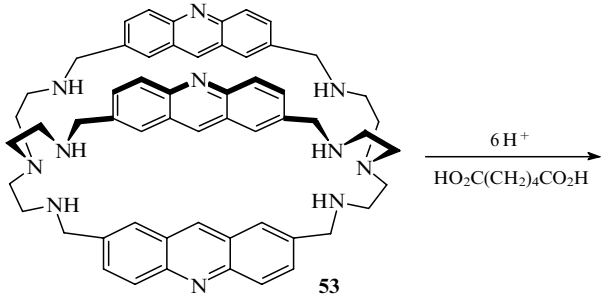
51

Compound **52** is an example of molecular sensor for amino acids.[87] In this compound, the bifunctional receptor is suitable for coordinating a zwitter-ionic amino acid molecule. The fluorescence of the anthracene fragment increases severalfold due to complexation.

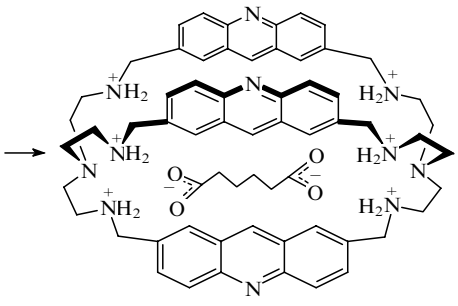


52

Polyazacycles are commonly used as selective sensors for anions. At pH 6, six of the eight nitrogen atoms in the cage of compound **53** are protonated (except the two apical ones). In this case, the fluorescence of the acridine fragment is quenched almost completely. When a dicarboxylate anion of suitable size is incorporated into such a protonated cell, intramolecular isolation

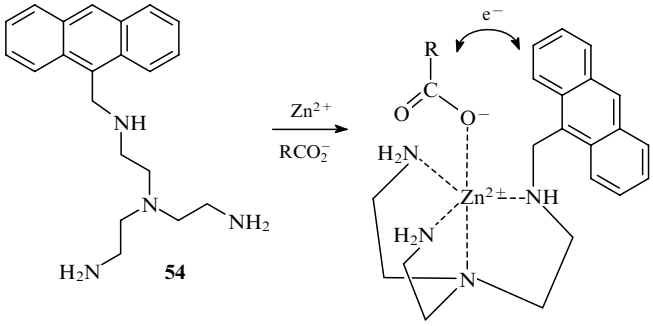


53



of the acridine rings occurs; the latter can no longer form an excimer and hence show strong one-ring fluorescence.[88]

An anion may also be fixed by a cation incorporated into the receptor and capable of coordination. For example, the tetramine **54**, which is a well-known chemosensor for zinc ions, displays secondary sensor capabilities in the presence of aromatic carboxylate anions.[89]

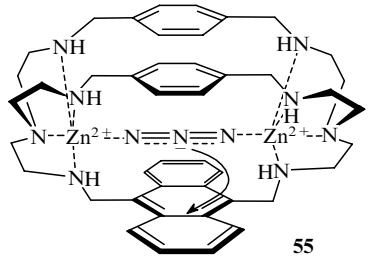


The fluorescence of the excited anthracene fragment is quenched when the carboxylate anion is bound with Zn^{2+}, which is explained [89] by electron transfer between the aromatic moiety of the carboxylic acid and the anthracene fluorophore.

The SO_4^{2-} ions can be determined selectively in acidic aqueous media using a complex of 1,4,8,11-tetrakis(naphthylmethyl)-1,4,8,11-tetraazacyclotetradecane with Cu^{2+}. The fluorescence intensity of this system increases in the presence of sulfate ions.[90]

A number of calix[4]pyrroles bound with anthracene moieties were synthesised and used as fluorescent chemosensors for anions (F^-, Cl^-, $H_2PO_4^-$).[91, 92]

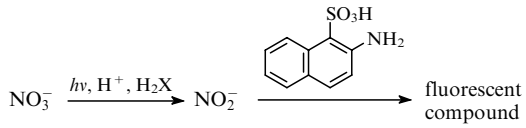
A bulky dizinc octamine complex **55** suitable for the selective determination of a number of anions was synthesised.[93] At pH 8 this complex reacts with ambident anions to give stable 1 : 1 adducts. The cavity of the molecule containing two zinc cations can accommodate linear anions such as N_3^- (2.34 Å), NCO^- (2.42 Å), and (partially) NCS^- (2.75 Å). If any of these anions is added to the sensor, fluorescence of the anthracene moiety is quenched due to electron density transfer.



55

Certain other anions, such as NO_3^-, HCO_3^-, SO_4^{2-}, Cl^- and Br^-, do not affect the fluorescence intensity of the anthracene moiety even if they are present in tenfold excess.

Other, less bulky molecular systems can also be effective for the determination of anions. In particular, Sharma and Street [94] reported a fluorescent determination method for nitrate and nitrite ions in water using simple photoreactions resulting in a fluorescent compound with unknown structure. This method is used for monitoring the content of NO_3^- anions in tap water.



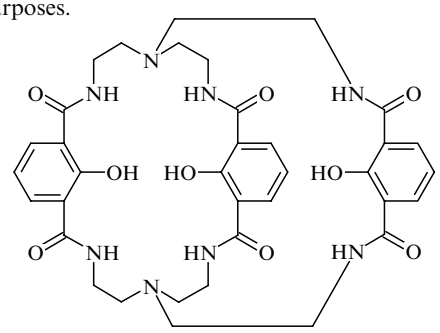
X = S^{2-}, SO_3^{2-}.

A method for the quantitative determination of nitrite ion in water and foodstuffs was elaborated [95] based on quenching of the indole fluorescence upon its interaction with nitrite ions in acidic medium. The detection limit is 2.5 mg per litre of the solution.

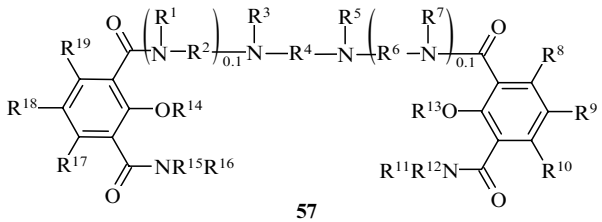
IV. Luminescent sensors for molecules

In Section III, we have already considered luminescent sensors for the determination of amino acids in acidic media [87] and dicarboxylic acids in alkaline solutions.[88] Recently, intense development of methods for the analysis of neutral organic molecules belonging to various classes has started. A number of sensors based on cationic and anionic receptors have been created for their determination.

For example, the luminescent sensor **56** has been patented; its non-cyclic analogue **57** has also been synthesised.[96] Complexes of these compounds with lanthanide cations are luminescent; the active cavities and diverse radicals $R^1 - R^{19}$ at the periphery of the macromolecules make it possible to detect a number of organic compounds, including peptides, nucleic acids and enzymes, and also to use these systems as luminescent markers for various purposes.

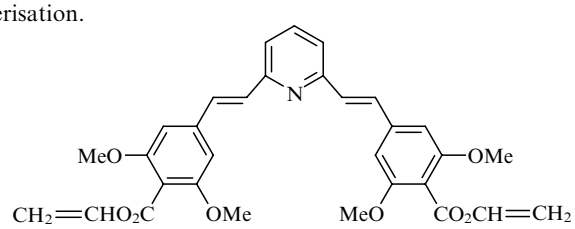


56



57

The fluorescent monomer **58** has been developed for the selective determination of phenols and anilines in non-polar solvents, even in the presence of aliphatic alcohols and amines, oxygen, and water.[97] The monomer can be involved in copolymerisation.



58

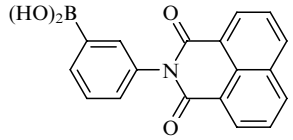
A new sensitive fluorimetric method for the determination of formaldehyde is based on the quenching of fluorescence of the aluminium complex of a tetra-substituted aminophthalocyanine in the presence of sulfite and formaldehyde. The latter can be determined at a concentration of 0.040 – 1.19 μg ml^{-1}, the detection limit being 7.5 ng ml^{-1} (see Ref. 98).

In order to determine traces of aldehydes and ketones in water, a fluorescent sensor was suggested, *viz.*, 2-aminooxy-*N*-(3-dansylaminopropyl)acetamide.[99] It can be used for identification of formaldehyde, acetaldehyde, acetone, and other aldehydes and ketones at concentrations < 1 μmol $litre^{-1}$. The very low detection threshold makes this method suitable for the analysis of snow, ice and water in clouds for the content of carbonyl compounds.

The content of hydrogen peroxide in snow and ice can be determined with high accuracy using a new chemiluminescent reagent, *viz*., 7-(4,6-dichloro-1,3,5-triazinylamino)-4-methylcoumarin.[100] The chemiluminescence intensity is directly proportional to the concentration of H_2O_2 in the range 1×10^{-1}–4×10^{-4} mol litre^{-1}. The majority of non-transition metals do not interfere with this analysis.

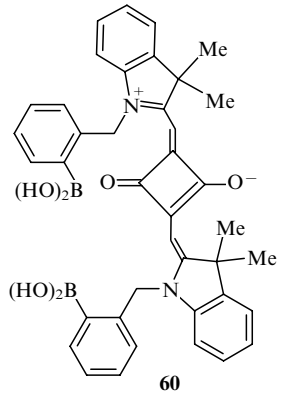
The first fluorescent sensor for the determination of boronic acids based on an anthracene fluorophore was created; a diethanolamine fragment was used as the receptor in this sensor. Complexation increases fluorescence by a factor of 19 due to the PET.[101]

Synthesis of a new water-soluble reagent **59** for carbohydrates based on 3-aminophenylboronic acid and naphthalene-1,8-dicarboxylic anhydride was reported.[102] Naphthalimide is the fluorophore in compound **59**. Significant change in the irradiation intensity ($I/I_0 = 0.25$) makes compound **59** a useful sensor in neutral media.[102]



59

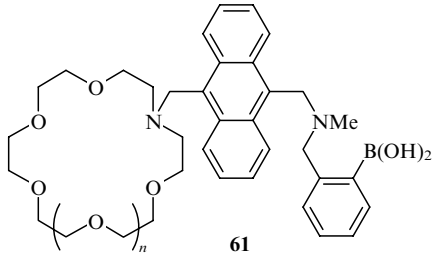
The symmetrical molecule **60** with two phenylboronic acid residues allows one to detect carbohydrates in aqueous solutions owing to a considerable enhancement of fluorescence.[103] Its characteristic feature is a low-frequency range; $\lambda_{max} = 645$ nm, with a shoulder at $\lambda = 695$ nm.



60

A fluorescent sensor for certain choline phospholipids was obtained based on squaramide.[104]

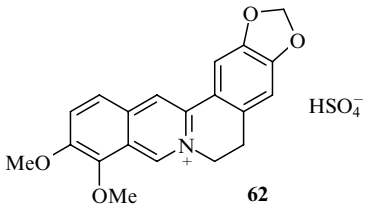
The selective fluorescent sensor **61** for D-glucosamine contains two receptors per molecule: monoaza-18-crown-6 (or monoaza-15-crown-5) and a boronic acid residue.[105]



61

$n = 0, 1$.

Fluorescent sensors were found even for such chemically inert organic compounds as hydrocarbons. For example, alkanes increase the fluorescence of berberine sulfate **62** under monochromatic UV irradiation. This effect was explained [106] by ion–dipole interaction of the hydrocarbon with berberine sulfate.

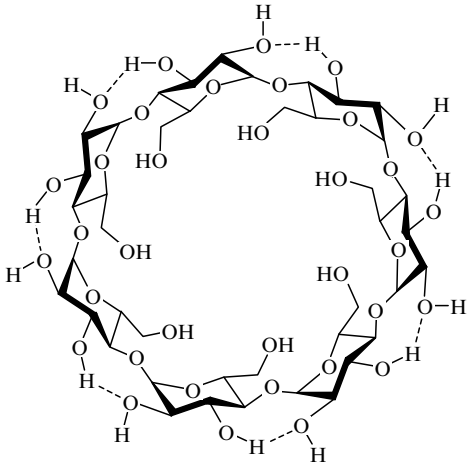


62

A method for selective determination of certain polycyclic aromatic hydrocarbons was suggested, involving the recording of the phosphorescence of sodium dodecyl sulfate micelles in the presence of acridine dyes (as donors of triplet energy) and polycyclic compounds (pyrene, anthracene, *etc*.) as acceptors.[107]

Cyclodextrins (CD) are also of considerable interest as chemosensors. A cavity in a cyclodextrin has low polarity, and its size is suitable for many 'guest' molecules. The properties of the substrate in the complex change considerably; this is reflected in the absorption and emission electronic spectra. Cyclodextrins are valuable sensors, as they often form water-soluble complexes owing to the presence of hydroxy groups; this expands considerably their scope.

More than 30 years ago, an inclusion complex was obtained, consisting of β-cyclodextrin **63** and 8-amino-1-naphthalenesulfonic acid. The molecules of the latter in the bound state showed intense fluorescence.[108] Later, a series of fluorescent sensors were obtained on the basis of this complex.



63

Two types of fluorescence, namely, monomer and excimer fluorescence, were studied for inclusion complexes of various naphthalene derivatives with β-CD.[109] Excimer fluorescence predominates for equimolar concentrations of naphthalene and β-CD. Complexes of 2,7-dimethylnaphthalene and 2-benzylnaphthalene with β-CD do not show excimer fluorescence.

Structures of various complexes of β-CD with naphthalene, phenanthrene, fluorene and cyclohexane were studied both by experimental and theoretical methods.[110–112] The complexation energy ranges within 9–12 kcal mol^{-1}.

Long-lived fluorescence at room temperature was found and studied for 2 : 2 complexes of β-CD with naphthalene.[113]

De la Pena *et al*.[114] studied the effect of various factors on the phosphorescence of the complex of α-CD with 6-bromo-2-naphthol in deaerated aqueous solutions at room temperature. Emission maxima were detected at $\lambda = 500$ and 535 nm. The determination threshold of bromonaphthol is 0.26 mg litre^{-1} with a standard deviation of 4%.

It was found subsequently that the addition of small amounts of various non-polar liquids (particularly cyclohexane) results in a very strong enhancement of phosphorescence. However, the presence of reducing agents (sodium sulfite) quenches the signal.[115]

Hydroxypropyl-β-CD in aqueous media forms a supramolecular inclusion compound with 8-anilino-1-naphthalenesulfonic

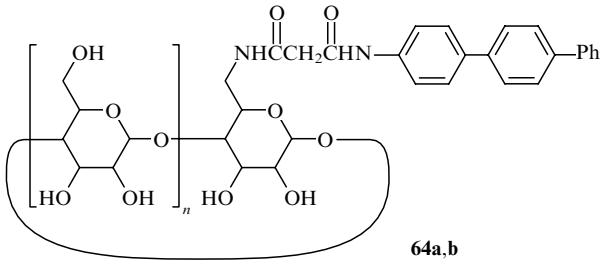
acid, which results in significant luminescence enhancement of the latter.[116]

Triethylenetetraminebis(β-CD) was synthesised from hydroxypropyl-β-CD and triethylenetetramine; after modification by Cu^{2+} ions, it showed specific luminescence upon interaction with 'guest' molecules, such as 6-(*p*-toluidino)-2-naphthalene- and 8-anilino-1-naphthalenesulfonic acids.[117]

A naphthol-modified β-CD was successfully used as a fluorescent sensor in the determination of trace amounts of CCl_4 and 2-methylisoborneol in water.[118]

β- and γ-Cyclodextrins modified by pyrrolinone residues are fluorescent chemosensors for a number of carboxylic acids, terpenoids and bile acids.[119] The cyclodextrin 'host' has a fluorescence band at $\lambda = 472$ nm, the intensity of which decreases if adamantane-1-carboxylic, *p*-aminobenzoic, benzoic, phthalic or cyclohexenecarboxylic acid is added as the substrate in aqueous medium at pH 5.90. However, if these acids are added in a buffer solution with pH 9.09, fluorescence is enhanced. The same effect is achieved if terpenoids, amino compounds and bile acid salts are added as the 'guests'.

The sensitivity of the cyclodextrin 'host' to the nature of the 'guest' molecules can be varied by changing the cavity size in the 'host'. For example, the terphenyl-substituted β-cyclodextrin **64a**, which has a smaller cycle than the γ-cyclodextrin derivative **64b**, 'recognises' well small terpenoid molecules, especially in the dimethyl sulfoxide–water medium (1 : 9). Bulkier bile acids are detected with lower sensitivity. It is interesting to note that the radiation intensity of cyclodextrin **64a** increases due to interactions with 'hosts', whereas that of compound **64b** decreases.[120]



64a,**b**

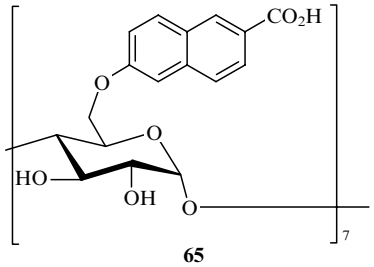
$n = 6$ (**a**), 7 (**b**).

Dansyl- and tosyl-modified β- and γ-CD are used as chemosensors for bile acids and terpenoids.[121] The luminescence of β-CD is quenched in the presence of 'guest' molecules, while that of γ-CD is enhanced as a result of interactions with monocyclic and non-cyclic molecules. Chenodeoxycholic acid, ursodeoxycholic acid, and (−)-borneol can be recognised with high sensitivity using β-CD, while γ-CD can be used to recognise lithocholic acid and (−)-borneol.

A system comprising a peptide, γ-CD and naphthalene fragments can also respond to the presence of various cholic acids due to the formation of a luminescent excimer.[122]

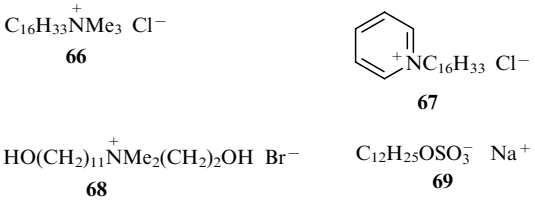
Mono[6-deoxy-6-(1-methyl-2-pyrrolidinylidenesulfamido)]-β-CD synthesised recently is also a promising sensor.[123]

A highly sensitive water-soluble fluorescent sensor system **65** was obtained; this is a β-CD (receptor) substituted with 2-naphthoic acid (fluorophore).[124]



65

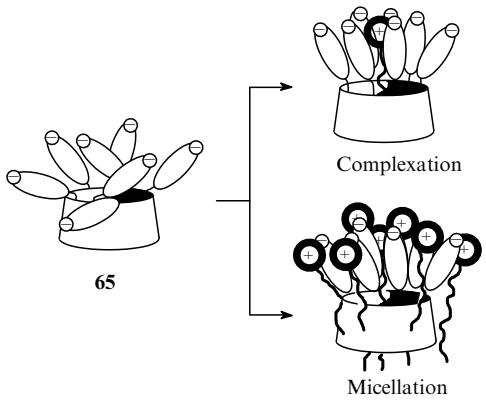
The sensor **65** was used to detect surfactants (mostly cations) of the types **66**–**69** with long hydrocarbon chains.



66 **67**

68 **69**

The fluorescence spectra of the sensor **65** undergo specific changes upon micellation or complexation.



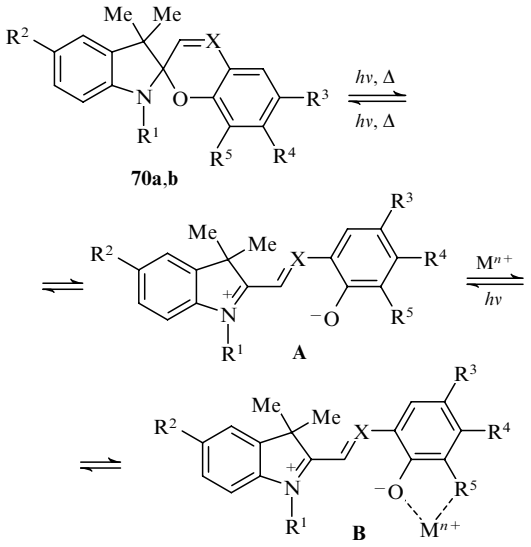
65

The nature of many sensor molecules involves a mechanism to control them, which makes it possible to turn on and off or switch the sensor process. When such systems are exposed to external factors (change in temperature, polarity, pH of the medium, concentration of metal ions, electromagnetic potential, chemical reactions), they undergo intramolecular rearrangements affecting the sensor properties. The following luminescent sensors can serve as examples: pH-controlled ones (azacrown ethers, polyaza compounds), those controlled by redox reactions (compounds **32**, **33**), pK^+- (compound **46**) and pNa^+-dependent (compound **44**).

V. Photochromic chemosensors

New highly sensitive photodynamic fluorescent sensor systems (*i.e.*, those that can be turned on and/or off upon irradiation of a solution) can be created based on photochromic spirocyclic compounds, such as spiropyrans **70a** and spirooxazines **70b**.

The general scheme of these transformations is shown below.



70a,**b** **A** **B**

X = CH (**a**), N (**b**); R^1–R^4 are various substituents, R^5 is complex-forming group.

Exposure of photochromic spirans **70a,b** to short-wave irradiation results in the merocyanine form **A**. The latter can undergo

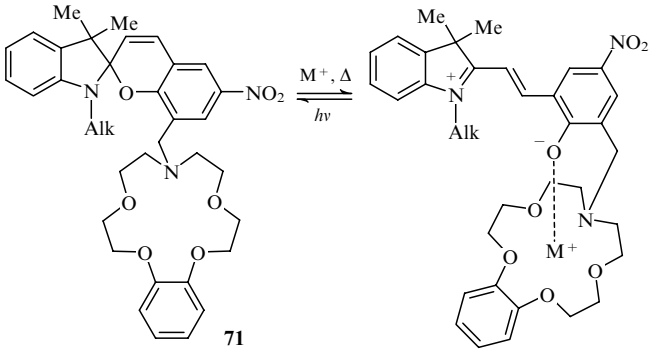
coordination with metal ions M^{n+} to give the complex **B** having specific absorption and fluorescence spectral characteristics different from those of the form **A**.

Studies of these systems as chemosensors started in the 1960s.[125,126] It was shown that complexes of such ions as Zn^{2+}, Co^{2+}, and Cu^{2+} with the spiropyrans **70a** have characteristic spectral bands in solution and can be used in analytical chemistry.

In 1982–1988, a number of papers were published (see, *e.g.*, Refs 127 and 128) reporting detailed studies on the complexation of various metal ions (Pb^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Cu^{2+}, Ce^{3+}, La^{3+}, *etc.*) with molecules of spiropyrans **70a** (R^1 = Me, R^2 = H, R^3 = H, NO_2, R^4 = H, R^5 = OMe) in organic solvents. The complexes **B** have characteristic bands in the absorption and emission electronic spectra. Certain cations coordinate the oxygen atom of the methoxy group and thus stabilise the open form. The open form **B** is also stabilised for $R^3 = NO_2$.

In solutions of spiropyrans **70a** with $R^1 = (CH_2)_2CO_2^-$ or $(CH_2)_2SO_3^-$, $R^2 = NO_2$, $R^3 = R^4 = R^5 = H$, the merocyanine form **A** is strongly stabilised by divalent metal ions (Zn^{2+}, Ca^{2+}). Specific fluorescence of solutions in acetone was noted.[129] Spiropyrans **70a** with R^1 = Me, R^2 = H, R^3 = H, NO_2, R^4–R^5 = N=CHCH=CH, which form **B**-type strongly fluorescent complexes with Mg^{2+}, Ca^{2+}, Ba^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+} and other cations, were found to be very sensitive sensors for these cations.

Incorporation of crown ether fragments as receptors into the molecules of spiro compounds changes the properties of these photochromic compounds. For example, nitrobenzospiropyran **71** containing monoazabenzo-15-crown-5 is a good Li^+ and Na^+ sensor with pronounced negative photochromism.[130]



71

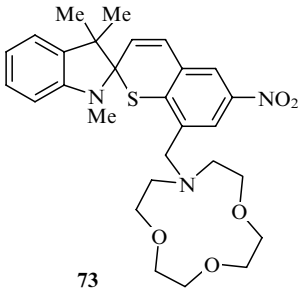
M = Li, Na, K.

Spiropyrans **70a** and spirooxazines **70b** with polyfunctional receptors undergo more complex transformations.[131–134] For example, for compounds **72a–c** there are two competing complexation pathways (Scheme 1) involving free alkaline-earth or rare-earth cations (structure **A**) or the same cations bound with the crown ether fragment (structures **B**, **C**). Each type of coordination is characterised by appropriate changes in the electronic spectra.

Complexation can be monitored coulometrically, by femtosecond spectrochromatography,[135] or this monitoring can be combined with mass spectrometric determinations.[136]

Light-sensitive membranes based on polyvinyl chloride with built-in fragments of lipophilic crown-containing spirobenzopyrans were obtained and studied. The photochromic parameters in such systems depend on the pH of the medium and on the concentration of alkali metal ions.[137]

The spirobenzothiapyran **73** containing the aza-12-crown-4 residue can form a complex with Li^+. The coloured photoinduced form of this compound has enhanced thermal stability, partially owing to stabilisation upon complexation.[138,139]

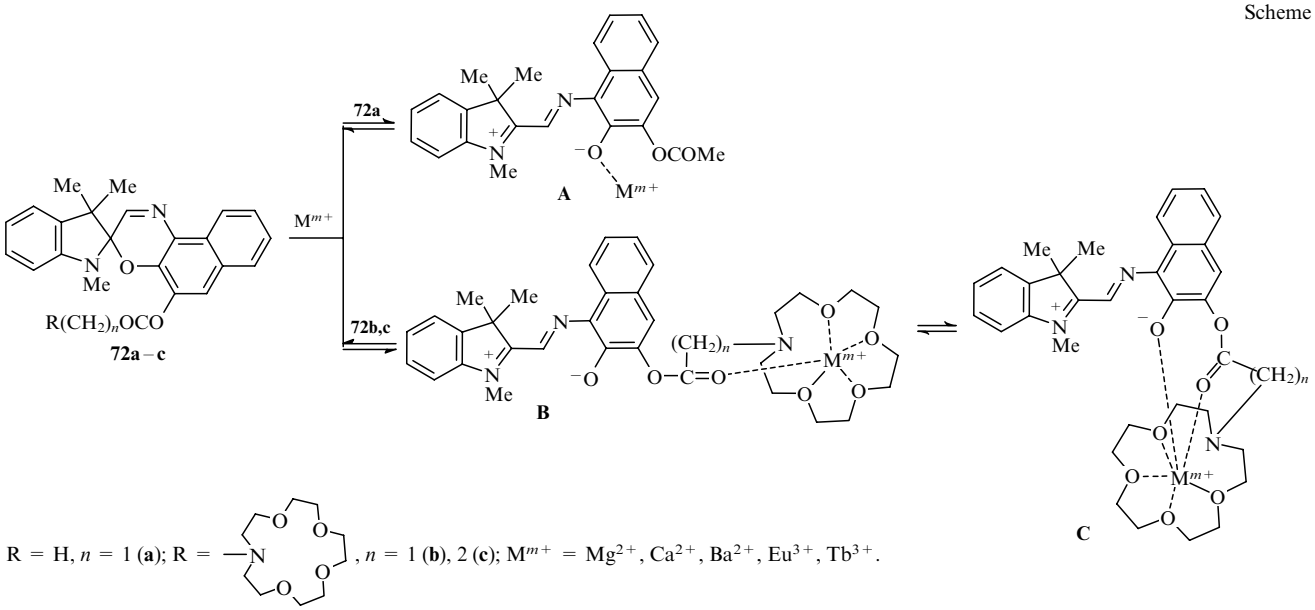


73

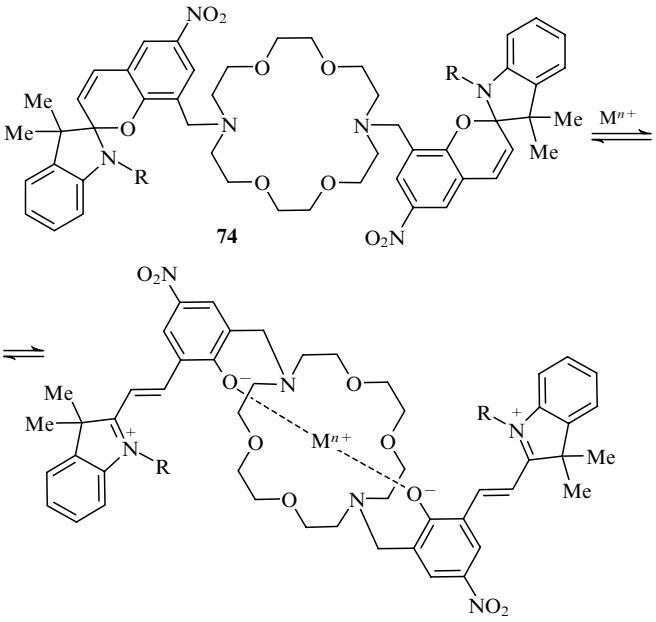
Stabilisation of an open merocyanine fragment also accompanies the complexation of Li^+ and especially Ag^+ with analogues of compound **73** containing monoaza-15-crown-5 and -18-crown-6.[139]

The two spirobenzopyran fragments linked with diaza-18-crown-6 (compound **74**) bind the Ca^{2+} ions more strongly than alkali metal cations due to an apical coordination of divalent cations by the anionic oxygen atoms of the ligand. This type of calcium complexation can be controlled by irradiation.[140]

Scheme 1

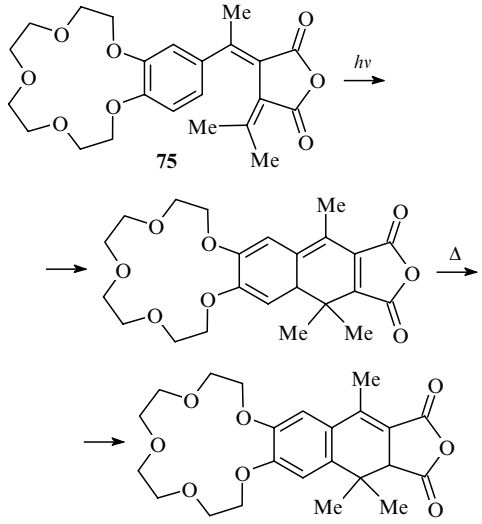


R = H, n = 1 (**a**); R = , n = 1 (**b**), 2 (**c**); M^{m+} = Mg^{2+}, Ca^{2+}, Ba^{2+}, Eu^{3+}, Tb^{3+}.



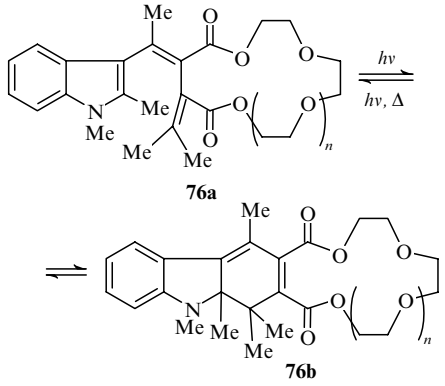
74

Upon complexation with Na^+, K^+ and alkaline-earth metal cations, the shift of the short-wave absorption band of phenylfulgide **75** containing a benzo-15-crown-5 fragment fused to the benzene ring was 28, 12, and > 40 nm, respectively, both in the open and cyclic forms.[141, 142]



75

Indolylfulgides **76** containing 14-crown-4, 17-crown-5 and 20-crown-6 fragments are sensors for Li^+, Na^+ and K^+, respectively; in this case, both the *E*- and *Z*-isomers of the open forms **76a** are more sensitive for alkali metal ions than the totally cyclic system **76b**.[143]

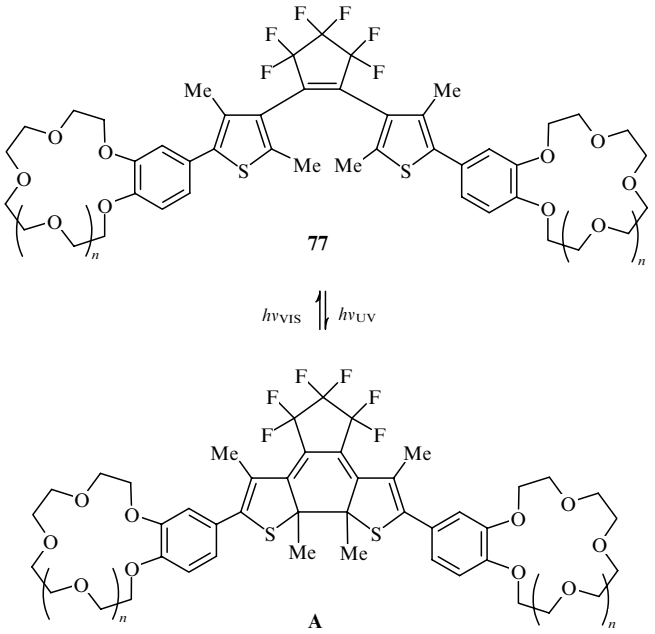


76a

76b

n = 1–3.

Dihetarylcyclopentenes **77** containing crown-ether fragments were synthesised and studied as photochromic sensors. These compounds can decrease considerably the degree of coordination of K^+, Rb^+ and Cs^+ when exposed to UV irradiation at a wavelength of $\lambda = 330 \pm 70$ nm (picrates in aqueous-organic media were analysed).[144–146] This phenomenon was explained by the ability of the original compound **77** to coordinate these cations by both crown-ether fragments simultaneously, whereas the more rigid photoreaction product, *viz*., isomer **A**, is devoid of this ability. The possibility of selective coordination of cations with certain radii is provided by the crown ether ring sizes.

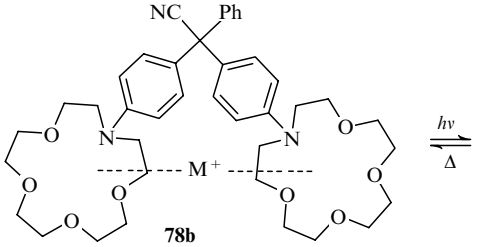


77

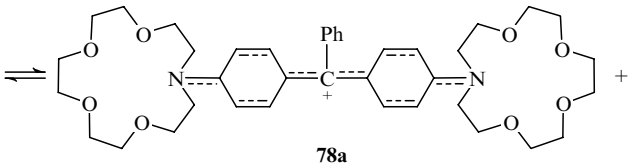
A

n = 0–2.

The novel photochromic compound **78a** based on a Malachite Green analogue containing two crown-ether fragments was synthesised.[147] Colourless complexes **78b** with metal cyanides are leuconitriles; their solutions are coloured reversibly under irradiation due to photodissociation.[147] The system **78** is a chemosensor for metal cyanides.



78b

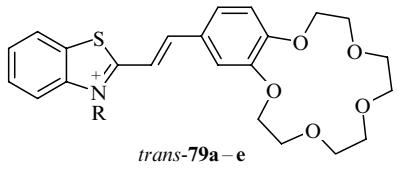


78a

$+ M^+ + CN^-$

Alfimov *et al.*[148–152] described crown-containing styryl dyes **79**, **80**, which are fluorescent sensors for alkaline-earth metal cations (Mg^{2+}, Ca^{2+}, Ba^{2+}).

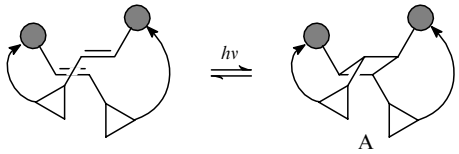
Compounds **79b–e** with *trans*-configuration of the double bond



trans-**79a–e**

R = $EtClO_4^-$ (**a**), $(CH_2)_2SO_3^-$ (**b**), $(CH_2)_3SO_3^-$ (**c**), $(CH_2)_4SO_3^-$ (**d**), $CH_2C_6H_4SO_3^-$ (**e**).

form (depending on the type of the substituent R, which serves as a spacer, and the nature of the counter-ion) either monomolecular complexes, in which the metal ion located within the crown is additionally coordinated by the sulfonic group oxygen, or type **A** dimers resulting from reversible [2 + 2]-cycloaddition.[148]



A

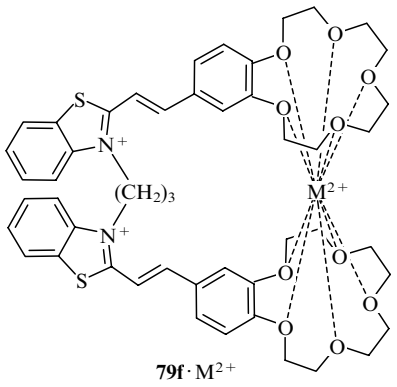
● — benzo-15-crown-5 fragment with a metal cation;

△ — benzothiazole residue; ↷ — $(CH_2)_nSO_3^-$ (n = 3, 4).

Illumination with light at a wavelength of 436 nm results in isomerisation of *trans*-complexes **79**·M^{2+} to give *cis*-complexes. The toluenesulfonic acid residue in the complex (*cis*-**79e**)·M^{2+} is arranged above the crown-ether plane to give a molecule 'capped' with the anion.[150]

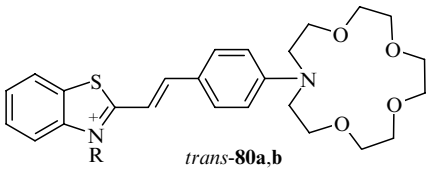
For dimeric molecules **79f** with a trimethylene bridge connecting the benzothiazole residues, the most stable configuration of the complexes is the structure **79f**·M^{2+} (see Ref. 149).

Quantum-chemical calculations of the energies of ground and excited electronic states of the molecules **79a–f**, their dimers and complexes confirmed the conclusions based on the experimental studies.[151]



79f·M^{2+}

The *trans*-**80a** dye containing the *N*-phenylaza-15-crown-5 fragment manifests a considerable ionochromic effect registered in electronic spectra (Fig. 4),[148] which, according to the calculated complexation constants, implies the usual complex structure where the Ca^{2+} cation is coordinated in the azacrown fragment.



trans-**80a,b**

R = $EtClO_4^-$ (**a**), $(CH_2)_3SO_3^-$ (**b**).

The data obtained for the complexation of compound *trans*-**80b** with Ca^{2+} and Zn^{2+} can be visualised schematically by the following sequence of equilibria

$$S{-}C + M \rightleftharpoons S{-}CM,$$

$$S{-}C + M \rightleftharpoons MS{-}C,$$

$$M(S{-}C)_{n-1} + S{-}C \rightleftharpoons M(S{-}C)_n,$$

$$MS{-}C + M \rightleftharpoons MS{-}CM,$$

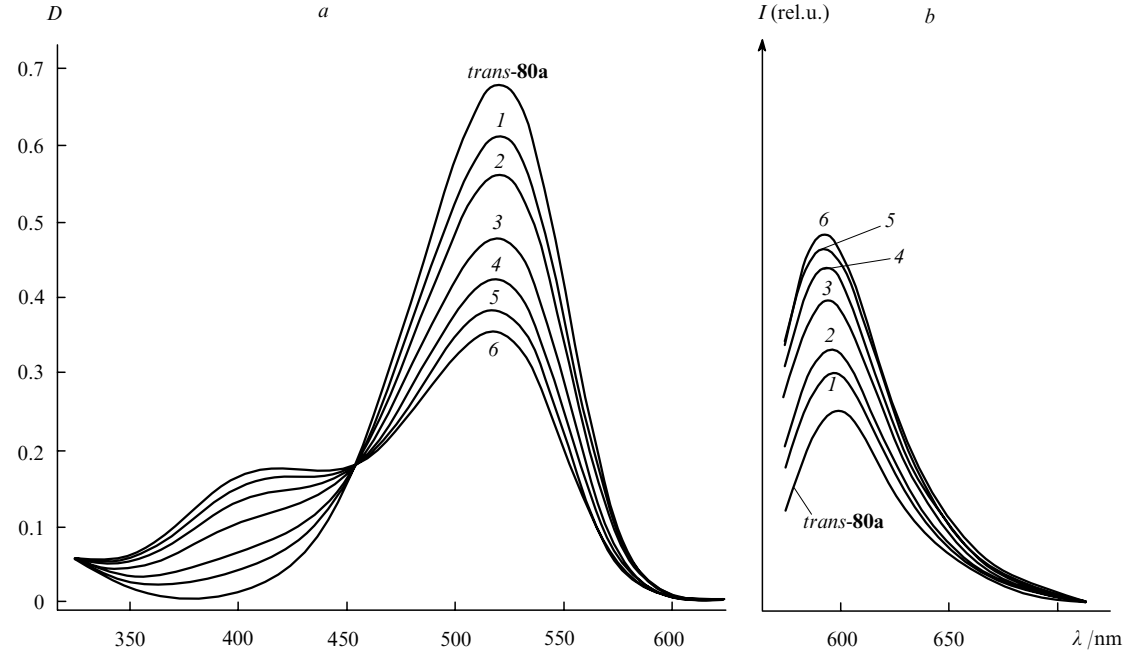


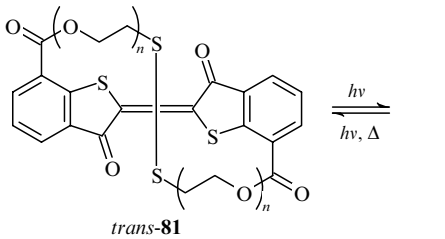
Figure 4. Dependence of absorption spectra (*a*) and fluorescence spectra (*b*) of ligand *trans*-**80a** ($c_{\mathbf{80a}} = 1.0 \times 10^{-5}$ mol litre^{-1}) in MeCN on the Ca^{2+} concentration at a constant concentration of ClO_4^- (0.01 mol litre^{-1});[148]
$c_{Ca2+} : c_{\mathbf{80a}}$ = 50 (*1*), 100 (*2*), 200 (*3*), 300 (*4*), 400 (*5*), 500 (*6*).

where S–C is a *trans*-**80b** molecule (S is a sulfonic group, C is an azacrown ether fragment); M is a metal ion, $n = 2-4$.

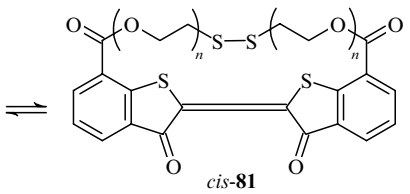
This means that, in addition to 1 : 1 complexes, the betaine **80b** forms aggregates comprising four dye molecules and one M^{2+} ion. Probably, the interaction between the metal cations with the sulfonic groups of the molecules makes the major contribution to the stability of these aggregates.[148]

Studies of ion exchange processes involving amphiphilic photochromic compounds **79** in the 'monolayer–aqueous phase' system showed that the Na^+, Ca^{2+} and Mg^{2+} ions increase the strain in the monolayer, whereas the K^+ ions decrease it considerably.[153, 154]

Compound **81**, which comprises thioindigo and dithiocrown-ether fragments, is a novel photochromic sensor for alkali metal cations and Ca^{2+}.[155] It exists as *cis*- and *trans*-isomers, each isomer having characteristic bands in the absorption spectra: $\lambda_{max} = 485$ and 545 nm for *cis*- and *trans*-**81**, respectively. The *trans*-isomer of compound **81**, which has weak coordinating properties, is transformed into the *cis*-isomer upon exposure to light with a wavelength of 550 nm;



trans-**81**

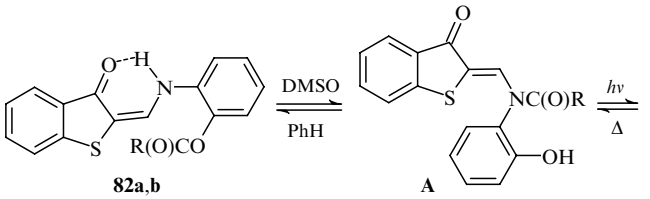


cis-**81**

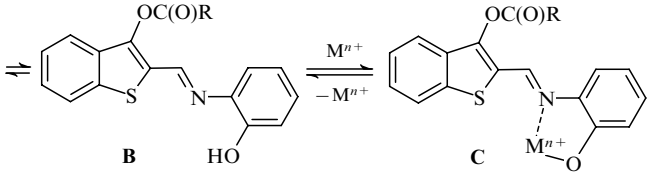
$n = 2, 3$.

the *cis*-isomer can coordinate a 'guest' cation. The complexation equilibrium constants of metal ions, determined by the extraction method, suggest a high sensitivity of the *cis*-isomer for Na^+, Cs^+ and Ca^{2+}; however, such ions as Hg^{2+}, Cd^{2+}, Cu^{2+}, Co^{2+} and Ag^+ do not form these complexes. The lifetime of the *cis*-isomer is hundreds times longer than that of its analogue (*cis*-thioindigo), even in the absence of metal ions.

We obtained and studied[156, 157] 2-(2-acyloxyphenylamino-methylene)-2,3-dihydrobenzo[*b*]thiophen-3-ones **82a**,**b**. These are solvato- and thermochromic compounds undergoing the following transformations.

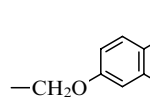


82a,**b** **A**



B **C**

R = Me (**a**),

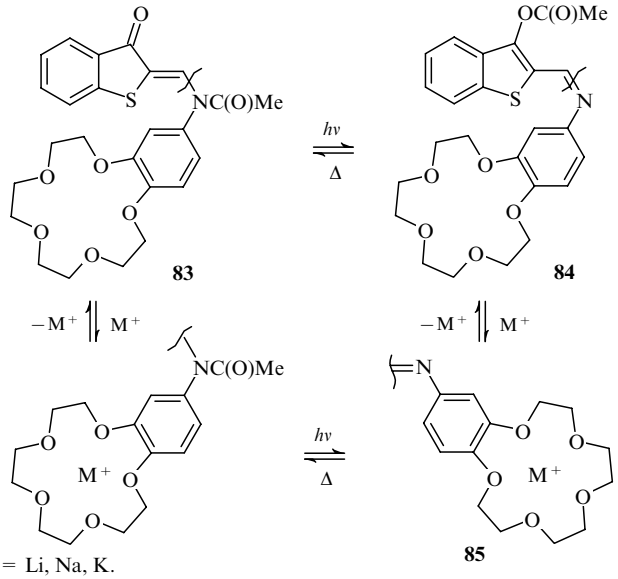


(**b**).

Under irradiation, the form **A** is transformed into the form **B**, thus creating conditions for the formation of the complex **C** with a metal ion; the spectral characteristics of the latter differ from those of compounds **A** and **B**, *i.e.*, the system **82** manifests metal-sensor properties. The acyl moiety can contain a fluorophore group, *e.g.*, the residue of 4-methylcoumarin-7-yloxyacetic acid (compound **82b**). It was shown by ^1H NMR and electronic spectroscopy[158] that an equilibrium is established in solutions between the original compound **82b** and the form **A**; the content of the latter increases with the solvent polarity. Illumination of the equilibrium mixture with light at 436 nm results in transfer of the acyl group from the nitrogen atom to the thiophene fragment. This produces an (*E*)-C=N bond. The absorption spectra of the system **82b** change if the solution contains Ca^{2+}, Mg^{2+}, Zn^{2+} or Ni^{2+} cations. However, the fluorophore residue does not behave as a luminescent indicator, probably because of preferential deactivation of excited molecules.

The system **83** comprising not only a benzothiophene fragment and an *N*-acyl residue but also an annelated crown ether can be used as a photochromic sensor for alkali metal ions.[159]

Illumination of compound **83** and its complexes with alkali metals with light at 436 nm results in migration of the acyl group from the nitrogen atom to the oxygen atom to give *O*-isomers **84** and **85**, respectively. Complexation with lithium ions results in the biggest changes in the absorption spectra.



83 **84** **85**

M = Li, Na, K.

Figure 5 shows a plot of the optical density of a solution of the complex **85** *versus* the concentration ratio of LiI and the ligand **84**

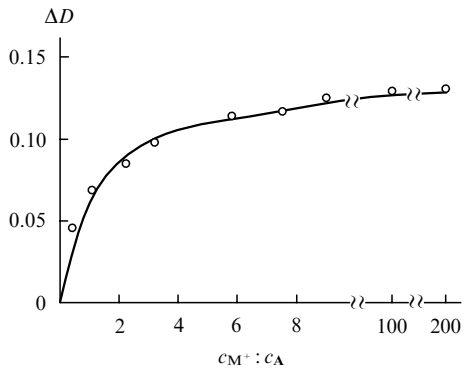


Figure 5. Dependence of the optical density variation (ΔD) of a solution of the complex **85** on the LiI (c_{M^+}) and the ligand **84** (c_A) concentration ratio.[159]

at the absorption wavelength of the complex ($\lambda = 357$ nm) upon addition of lithium iodide to an illuminated solution of the *O*-acetyl form of **85** (at a concentration of 6.55×10^{-5} mol litre^{-1}). The maximum extinction is reached at a tenfold excess of LiI. This specific behaviour of this system and its high sensitivity for Li^+ make it possible to place it among photochromic sensors.[160]

VI. Conclusion

Thus, recent studies demonstrate a considerable interest in the creation of novel chemosensor systems applicable to the analysis of inorganic and organic substrates. Table 1 shows the characteristics of certain organic sensors.

Table 1. Characteristics of certain organic sensors.

Compound	Substrate	Detection threshold /mol litre^{-1}	Analytical fluorescence wavelength /nm	Ref.
1c	Ca^{2+}	1×10^{-6}	333	15
1c	Ba^{2+}	1×10^{-6}	333	15
4a	Ca^{2+}	3×10^{-6}	417	24
4b	Ca^{2+}	3×10^{-6}	404	24
7a	Mg^{2+}	1×10^{-8}	530	27
7b	Hg^{2+}	1×10^{-8}	476	27
20	Ce^{3+}	2×10^{-6}	406	46
20	Nd^{3+}	2×10^{-6}	406	46
30c	Zn^{2+}	1×10^{-6}	416	55
30c	Hg^{2+}	5×10^{-7}	416	55
32	Hg^{2+}	1×10^{-5}	413	58
33	Cd^{2+}	1×10^{-5}	413	58
36a	Zn^{2+}	3×10^{-8}	514	62
36b	Zn^{2+}	1×10^{-8}	514	62
38	Co^{2+}	5×10^{-7}	514	65
40	Ni^{2+}	5×10^{-8}	400	80
45	Na^+	6×10^{-6}	480	74
47a	K^+	1×10^{-6}	427	79
47b	Cs^+	1×10^{-8}	429	79
48	Cu^{2+}, Ni^{2+}	5×10^{-8}	400	80
49 ($m = 4$, $n = 3$)	Cd^{2+}	2×10^{-7}	520	81
	Co^{2+}	1×10^{-7}	520	81
51	$H_2PO_4^-$	2×10^{-6}	377	86
51	HSO_4^-	3×10^{-6}	377	86
59	D-fructose	1×10^{-3}	400	102
84	Li^+	2×10^{-5}	357 [a]	159
Indole	NO_2^-	2.5 [b]	350	95
α-CD	6-bromo-2-naphthol	0.04 [c]	500	115

[a] Absorption band; [b] μg litre^{-1}; [c] mg litre^{-1}.

Currently, diverse types and classes of both organic and inorganic compounds are used as abiotic sensors or substrates. The use of crown-ether compounds as receptors stimulated the creation of chemosensors based on complex three-dimensional systems, including polyamines, dendrimers, calixarenes, cyclodextrins and their combinations.

Fluorescent chemosensors with high sensitivities and selectivities have been synthesised; the action of these sensors is based on specific but reliable intramolecular interaction mechanisms (the PET and PCT effects; excimers and exciplexes). Studies aimed at the external controlling of sensor processes are of current interest. The search for new types of molecular 'switches' is under way. Some chemosensor systems are created using elements of supramolecular chemistry and nanotechnologies; this makes it possible to create sensors with unique capabilities, *e.g.*, properties of molecular machines [52, 161] or artificial memory elements.[14, 52, 79]

The scope of application of fluorescent sensors expands: from routine laboratory reagents for cations and anions, they grow into systems for identifying complex organic molecules, analysing various biological substrates,[35, 55, 61] pesticides,[162] and foodstuffs,[163] monitoring the state of the atmosphere and oceans,[29, 164] *etc*.

Although the theory of chemical sensors has certain achievements,[165] it is developing somewhat more slowly than experimental and applied studies. The general theory of chemosensors requires new data on the mechanisms of intramolecular electronic interactions in the systems receptor – conductor – fluorophore, on the effects of external factors on the properties of sensors, on the nature of complementarity of receptors and substrates, *etc*.

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