Recognition elements for metal ions as parts of optical chemical sensors

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This paper focuses on chromoionophores and fluoroionophores immobilized or covalently attached in/on a matrix or support, respectively. Silica xerogel serves as the matrix and amino-modified silicate or mesoporous silicate (MCM-48) as the support. The studied materials prepared by sol-gel procedure can be treated as potential recognition elements for optical chemical sensors. Action of the recognition elements is based on absorption spectra changes or template effect for the chromoionophores and photoinduced electron transfer (PET) effect in the case of the fluoroionophores.

1. INTRODUCTION

In general, a *sensor* is a device that detects or measures a physical property and records, indicates or otherwise responds to it [1]. While, a *chemical sensor* is defined as a device this responds to a particular analyte in a selective way through a chemical reaction and can be used for the qualitative or quantitative determination of the analyte [2]. Other term used in the sensor area is *transducer*, defined as a device that converts an observed change (physical or chemical) into a measurable signal. In chemical sensors it is an optical signal whose magnitude is proportional to the concentration of a specific chemical or set of chemicals.

Recognition elements are the key component of any sensor device (Fig. 1). They impart the selectivity that enables the sensor to responds selectively to a particular analyte or group of analytes, thus avoiding interferences from other substances [3]. *Optical transducer* have taken a new lease of life with the development of fiber optics, thus allowing greater flexibility and miniaturization.

The techniques used include absorption, fluorescence, luminescence, internal reflection and surface plazmon spectroscopies as well as light scattering.
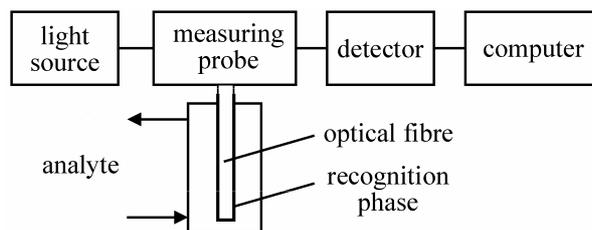

Fig. 1. Scheme of an optical chemical sensor. A recognition element is spread on an optical fiber.

1.1. Sensor molecules

After absorption of light, the excited molecule will decay in one of a variety of ways. If the molecule is has a suitable complex structure so that there is time for a radiatonless decay to the lowest excited singlet state, it can then re-emit radiation, usually at a lower wavelength than the original excitation. This phenomenon is known as *fluorescence*. The emitted fluorescent radiation can be measured in a similar way to UV-Vis radiation, and is also subject of the Beer-Lambert law. The method is often more sensitive than absorption spectroscopy. In addition, the change of wavelength has advantages in analysis.

The electronic transitions of organic molecules occur in the ultraviolet and visible regions of the electromagnetic spectrum. This phenomenon is responsible for *optical absorption*. The major modes of excitation consuming energy are as follows:

- $\sigma \rightarrow \sigma^*$ and $\pi \rightarrow \pi^*$, *i.e.* from bonding to anti-bonding molecular orbitals
- $n \rightarrow \sigma^*$ and $n \rightarrow \pi^*$, *i.e.* from non-bonding to anti-bonding molecular orbitals.

While such spectra can supply some information about the molecular structure, the major application is quantitative analysis, making use of the Beer-Lambert law.

Among the selective molecular elements are molecular systems exhibit fluorescence and absorption as *fluoroionophores* and *chromoionophores*, respectively. These systems are molecules of abiotic origin that signal generally the presence of matter or energy. The anatomy of a sensor molecule has the lumophore-spacer-receptor format [4, 5]. The receptor part of the molecule reversibly captures a representative of the analyte population if the latter is concentrated enough. The power of light absorption or emission possessed by the lumophore module enables it to perform the powered data transmission.

Fluoroionophores are molecules consisting of a *fluorophore* (the *signaling moiety*) linked to a *ionophore* (the *recognition moiety*). The *signaling moiety* acts as a signal transducer, i.e. it converts the information (recognition event) into an optical signal expressed as the changes in the photophysical characteristics of the fluorophore [6]. This type of molecules sense analyte concentration with fluorescence signal transduction based on the *photoinduced electron transfer*, PET, effect illustrated in Figure 2. These changes are due to the perturbation (by the bound cation) of one of the photoinduced processes such as electron transfer (as mentioned above) but also charge transfer, energy transfer, excimer or exciplex formation or disappearance, etc. The recognition moiety is responsible for selectivity and efficiency of binding which depend on the ligand topology, on the characteristics of the cation (ionic radius, charge, coordination number, hardness, etc.), and on the nature of the solvent (and pH, ionic strength in the case of aqueous solutions) [7].
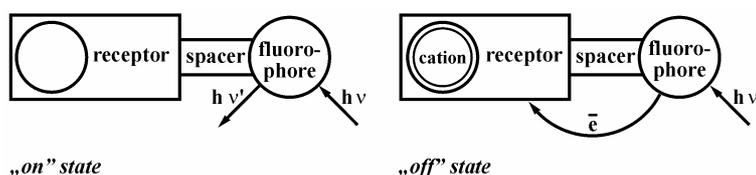

Fig. 2. Mechanism of PET signaling system (after ref. 9)

In our case are employed fluoroionophores based on cation control of photoinduced electron transfer (PET sensors). The design of such sensing molecules requires special care [8]. In this class of fluorophores, distinction is to be made according to the structure of the complexing moiety: chelators, podands, coronands (crown ethers), cryptands, calixarenes.

A distinct advantage of PET acting molecules is the very large change in fluorescence intensity usually observed upon cation binding, so that the expression "off-on" and "on-off" fluorescent sensors is often employed. Another characteristic is the absence of shift of the fluorescence or excitation spectra which precludes the possibility of intensity-ratio measurements at two wavelengths.

The molecular device is powered by the excitation light. It loses the excited state energy by transferring an electron from the receptor module to the lumophore. The opposite direction is also perfectly exploitable if required by the designer. In the simple instance the electron transfer is essentially reversed immediately following excitation. Such self-repair is essential following a potentially lethal PET process so that the molecular system is reasonably

photostable. The important net result for us is that no luminescence is seen following excitation. This is the "off" state of the molecular switch.

The situation change sharply the moment the receptor module within the molecular system captures the chosen analyte (which is a cation for the purposes of illustration). Again, if we consider excitation of the lumophore module, we find the analyte influences the transferring electron. At the simplest level, it is due to electrostatic charge attraction between the jumping electron and the captured analyte. So the photoinduced electron transfer is arrested and the unusewd energy of the excited state is dumped as a luminescence photon. This is how the analyte population is visualized. Now we have the "on" state of the molecular switch [9].

Ionochromism is the name applied to the phenomenon of a colour change associated with the interaction of compounds or materials with an ionic species. The organic structures that undergo the colour change on interaction with the ions are called *chromoionophores*. They act with optical absorption signal transduction. It means that the colour change can be from colourless to coloured or coloured to colored and is usually reversible. A closely related topic is that of fluoroionophores, where ions cause a change in the fluorescent emission of the molecule.

Metal ions, especially transition metal ions, form coloured complexes with chelating ligands that are basis of the analytical methods and indicators for these ions that have been used for many decades [10-12]. The term metallochromism has been applied to this phenomenon, and hence metallochromic indicators. Typical bidentate ligands are dimethylglyoxime, 1,2-dihydroxybenzenes and 1-hydroxyanthraquinones, 8-hydroxyquinoline, 2,2'-bipyridine and σ-phenantroline, and tridentates include σ-σ'-dihydroxo dyes, and multi-dentates such as formazans. The combination of complex forming colored dyes, e.g. Eriochrome Black T, with the complexing agent EDTA is used for the estimation of variety of metal ions [13].

Following the Nobel prize winning discovery by Pedersen in 1967 of crown ethers and their ability to form complexes with alkali metal ions, there has been a tremendous amount of work on complex forming behaviour of these materials [14, 15]. To make these crowns more strongly coloured, and hence more widely applicable as indicators or chromoionophores, chromophores such as azos and indoanilines have been attached to the ring; the crown ring size determining which metal ions can coordinate [16, 17].

1.2. Matrices or supports for sensor molecules

One of the chief advantages of *sol-gel processing* is that processing temperatures can be reduced compared with more traditional methods. This has led to improvements in the preparation of amorphous materials, with respect to

doping and additives which previously would have been limited to inorganic compounds which could withstand elevated glass melt temperatures. During the last years, the sol-gel process has been used to incorporate an ever increasing list of organic species into inorganic media for particular use from our point of view as sensing materials [18].

Beyond the advantages of low (and thus compatible) thermal processing, sol-gel derived glass hosts are more thermally, chemically, and photochemically stable than plastic carriers which had been the only materials used as hosts. In addition, the guest molecules are better protected and non-leachable, thus leading to lower photodegradation rates [18]. Although such improved properties for organic species incorporated into sol-gel matrices have been reported, a basic understanding of how structure evolves and its impact on the resultant properties is not yet fully understood. From our point of view the most interesting line of research in this field is the fabrication of composites with specific optical properties based on the organic additive [19].

Avnir et al. [20] were the first to report the incorporation of an optically active organic molecule (rhodamine 6G) into a sol-gel derived silica host. Since that time, there have been many other organic dopants investigated; and the variety of properties and applications that are attainable from this method may only be limited by ones imagination given the vast spectrum of organic compound that exist. Applications that have been investigated to date include among others various types of transducer for chemical optical sensors [21, 22].

Both the molecular selective elements (*vide ultra*) must be connected to the transducer. There are two methods used in our case, namely:

- *Entrapment*, where the selective element is trapped in a matrix of gel, paste or polymer – this is a very popular method.
- *Covalent attachment (grafting)*, where covalent chemical bonds are formed between the selective component and the transducer – preferred in our experiments.

The most important characteristic of sensors is *selectivity*, i.e. the ability to discriminate between different substances. Such behaviour is principally a function of the selective component, although sometimes the operation of the transducer contribution to the selectivity.

2. EXPERIMENTAL

2.1. Recognition elements prepared by entrapment

2.1.1. *Chromoionophores.* We are interested in developing materials, which are able to recognize metal ions in aqueous solutions. The recognition materials consist of chromoionophores (shown in Fig. 3) entrapped in a porous xerogel matrix by sol-gel procedure [23]. Very often silica xerogel plays a role of host

matrix for organic molecules with sensor function [24-26]. In our paper [27] studies on optical absorption of chemical recognition elements for potential optical absorption sensors based on chromoionophores entrapped in silica xerogel are described (*vide infra*).

Each of the chromoionophores (Fig. 3) entrapped in silica xerogel exhibits distinctive spectral changes in UV range due to coordination with at least one of the metal ions from the following groups of metals: alkali (Li^+, Na^+, K^+ and Cs^+), alkaline earth (Mg^{2+}, Ca^{2+} and Ba^{2+}), heavy (Cd^{2+}, Sn^{2+} and Pb^{2+}) and transition (Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}) ions. The most distinctive reflectance spectral changes for some metal ions are shown in Figures 4A-D. Hence, Cs^+ ion complexed with the ligand 1 shows quite dissimilar reflectance spectrum than the other cations of the alkali group and the free chromoionophore (Fig. 4A). Similarly, spectrum of ligand 1 undergoes specific change after coordination with Mg^{2+} (Fig. 4B). On the other hand, chromoionophore 3 distinguishes Sn^{2+} from Cd^{2+} and Pb^{2+} by spectral change, as illustrated in Figure 3C. Chromoionophore 4 embedded in silica differentiates spectrally Cu^{2+} ions comparing changes caused by Co^{2+}, Ni^{2+} and Zn^{2+} in aqueous solution (Fig. 4D).
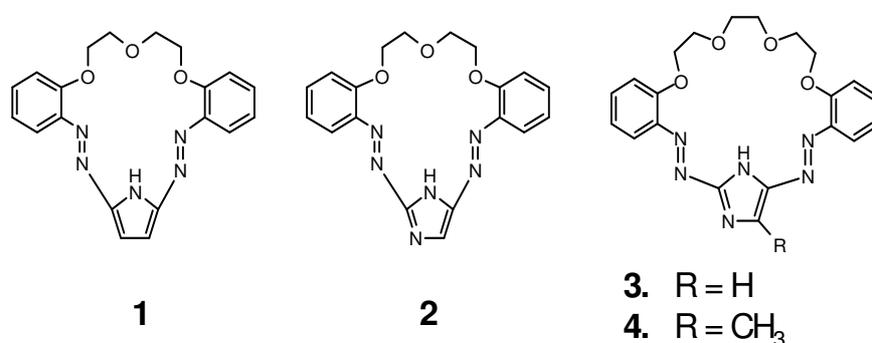

Fig. 3. 18-Membered macrocyclic derivative of pyrrole 1 and imidazole 2 (see ref. 28) and new synthesized 21-membered chromogenic derivatives of imidazole 3 and 4-methylimidazole 4.

The chromoionophores shown in Figure 3 are molecules with extended framework consisting of a σ-bonding set and an associated conjugated π-system. The lower energy electronic transitions occur, when an electron is promoted from an occupied π-orbital to an unoccupied π* orbital. It is generally assumed that the low energy π-π* transitions are principally responsible for UV and visible light absorption [29]. The π-π* transitions for organic dyes, which involve considerable charge transfer in donor-acceptor chromogens, are highly probable. Therefore, it gives rise to intense optical absorption in UV-visible range.
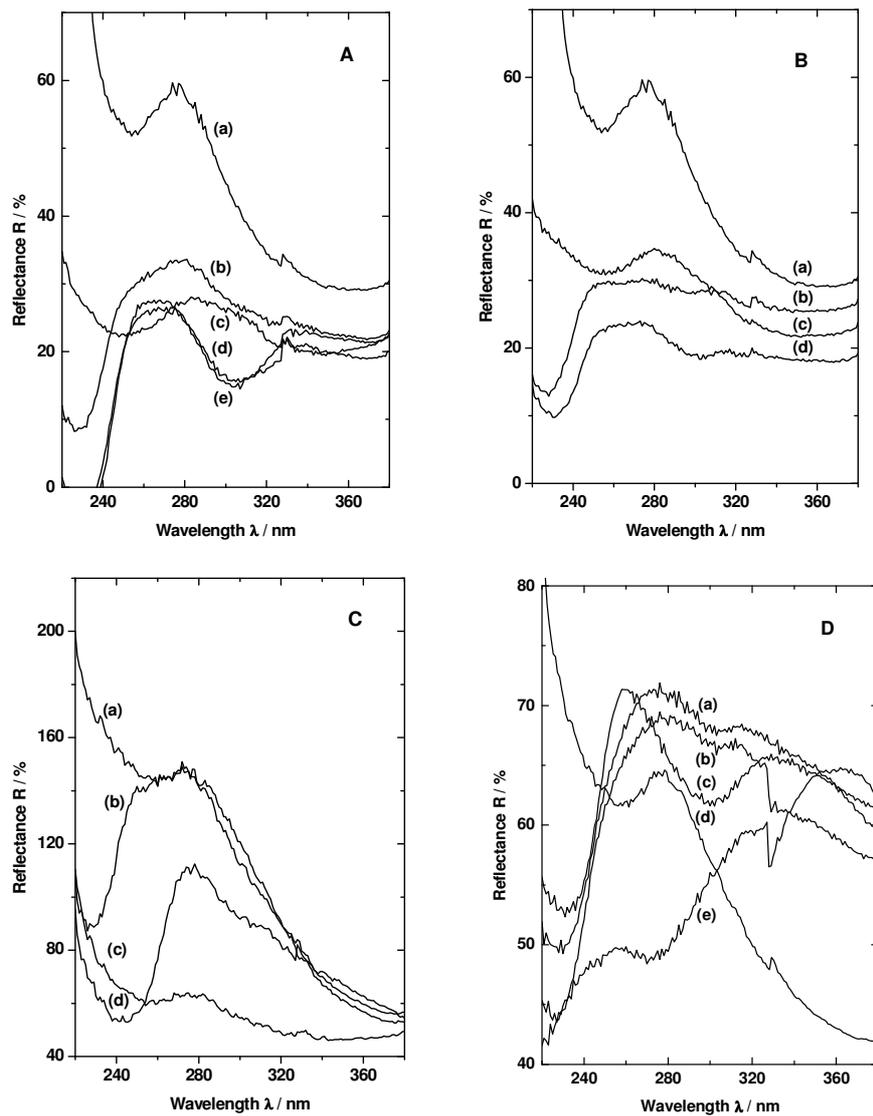
Fig. 4. Reflectance absorption spectra of chromoionophores immobilized in silica xerogel and complexed with metal ions. A. Alkali cations with ligand 1: (a) free ligand, (b) K^+, (c) Cs^+, (d) Li^+ and (e) Na^+. B. Alkaline earth cations with ligand 1: (a) free ligand, (b) Ba^{2+}, (c) Mg^{2+} and (d) Ca^{2+}. C. Heavy cations with ligand 3: (a) free ligand, (b) Cd^{2+}, (c) Sn^{2+} and (d) Pb^{2+}. D. Transition cations with ligand 4: (a) Ni^{2+}, (b) Co^{2+}, (c) Zn^{2+}, (d) free ligand and (e) Cu^{2+}.

Surprisingly, the spectral changes of 21-membered macrocycle 3 and 4 in xerogel matrix upon coordination of Li⁺ ions depend on molar ratio $x = $ [Li⁺] / [chromoionophore]. The spectra dramatically differ for the ratio lower or higher than 1. The respective spectra for 3 and 4 are collected in Figs 5A and B, respectively. Three of the bands at about 270, 320 and 360 nm are characteristic for the free ligands and the ligands complexed with Li⁺ if $x < 1$. However, if molar ratio x exceeds 1, additionally a typical band appears at 237 nm.

On the other hand, no drastic spectral changes are observed in the case of 18-membered macrocycle chromoionophores 1 and 2, when they coordinate Li⁺ ions at molar ratio x lower and higher than 1. It is shown as for example for 2 in Figure 5C. In the figure each spectrum consists of two bands but for solution with $x > 1$ a typical band at 237 nm appeared. In spectra of the free ligand and the ligand complexed with Li⁺, when $x < 1$ short wavelength bands partly overlap the typical 237 nm band.

2.2. Recognition elements prepared by covalent attachment

2.2.1. Chromoionophores. A chemical recognition phase for metal cations can be prepared by covalent bonding (grafting) of one of the chromoionophore molecules shown in Figure 6 on the silicate xerogel surface equipped in amino groups.

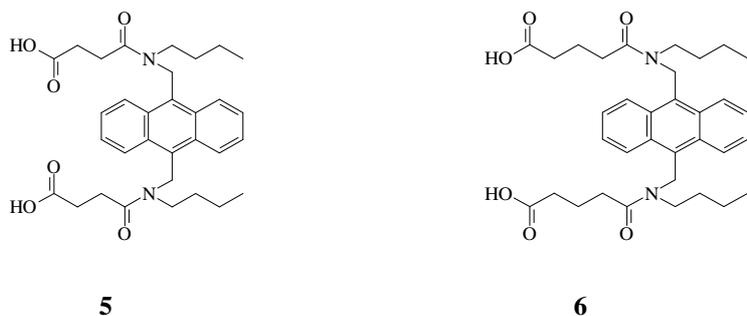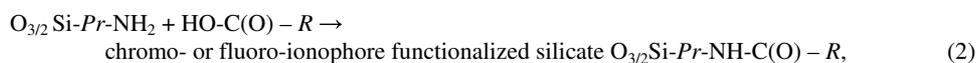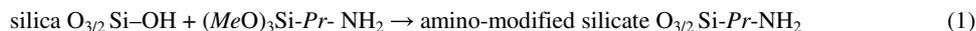**5**   **6**

Fig. 6. Molecular structures of chromoionophores with anthryl (5 and 6) or anthraquinone group (7) and two carbonyl groups able to be grafted on amino-modified silicate support.

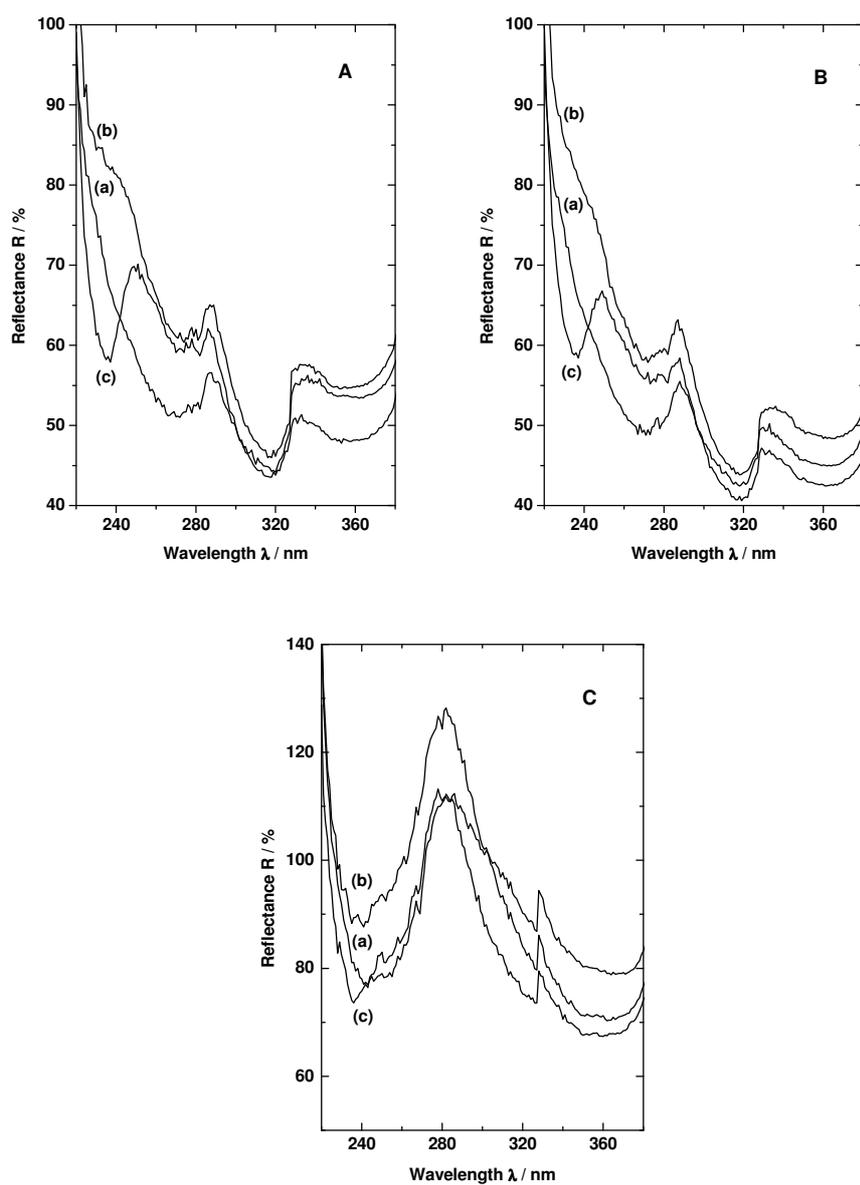The stable grafting of the chromoionophore is realized as in the following reaction scheme:

silica $O_{3/2}$ Si–OH + (*Me*O)$_3$Si-*Pr*- NH$_2$ → amino-modified silicate $O_{3/2}$ Si-*Pr*-NH$_2$ (1)

$O_{3/2}$ Si-*Pr*-NH$_2$ + HO-C(O) – R →

      chromo- or fluoro-ionophore functionalized silicate $O_{3/2}$Si-*Pr*-NH-C(O) – R,   (2)

Fig. 5. Reflectance absorption spectra of chromoionophores: A. 3, B. 4 and C. 2 encapsulated in silica xerogel and complexed with Li$^+$ ions: (a) free ligand, (b) $x < 1$ and (c) $x > 1$, where molar ratio $x = $ [Li$^+$]/[ligand].

where: *Me* and *Pr* are methyl and propyl groups, respectively, and *R* is chromo- or fluoro-ionophore fragment. Because the chromoionophores 5-7 are equipped with two grafting groups they form gate-like structures after grafting. These structures could serve as templates for ions of a chosen metal. In our experiment considering the template effect we try to prepare a template for Cu(II) ions. In each stage of the experiment reflection absorption spectra were recorded in order to observe the results (Figs 7A, B and C). Firstly the Cu(II) complex with the chromoionophore was grafted on the amino-modified silicate support. Characteristic spectra correspond to the grafted primary complex [see spectra (a)] in each chromoionophore case.

    In the second stage, the Cu(II) ions were removed by protonation and by this way the template for Cu(II) ion was formed [spectra (b)]. In third step the template systems were proved by such metal ions as Cu(II) – spectra (c), Co(II) – spectra (d), Ni(II) – (e) and Zn(II) – spectra (f) whether the template is really for Cu(II). Quite similar shape of spectra (a) and (c) in the case of chromoionophores 6 and 7 suggests that these compounds can form molecular cage suitable for Cu(II). In contrast, compound 5 does not exhibit the similarity of spectra (a) and (c). It is probably due to smaller size of its cage after grafting [30].

2.2.2. *Fluoroionophores*. There is the possibility of using techniques of sol-gel synthesis to produce a mesoporous silica matrix (*e.g.* MCM-48) and in the next stage to fabricate a chemical recognition phase for metal cations by covalent bonding of a fluoroionophore system on the silicate surface [31]. We show results of our studies on luminescence properties of the chemical recognition phase for a potential fluorescence chemical sensor, which is based on a pirene fluoroionophore covalently bonded to the synthesized cubic mesoporous silica with three-dimensional pore network [32]. The potential fluoroionophore compounds as a pirene derivatives, shown in Figure 8, possess a receptor fragment with donor atoms such as nitrogen and oxygen and carbonyl group able to graft to amino group on the mesoporous silica of the type MCM-48.
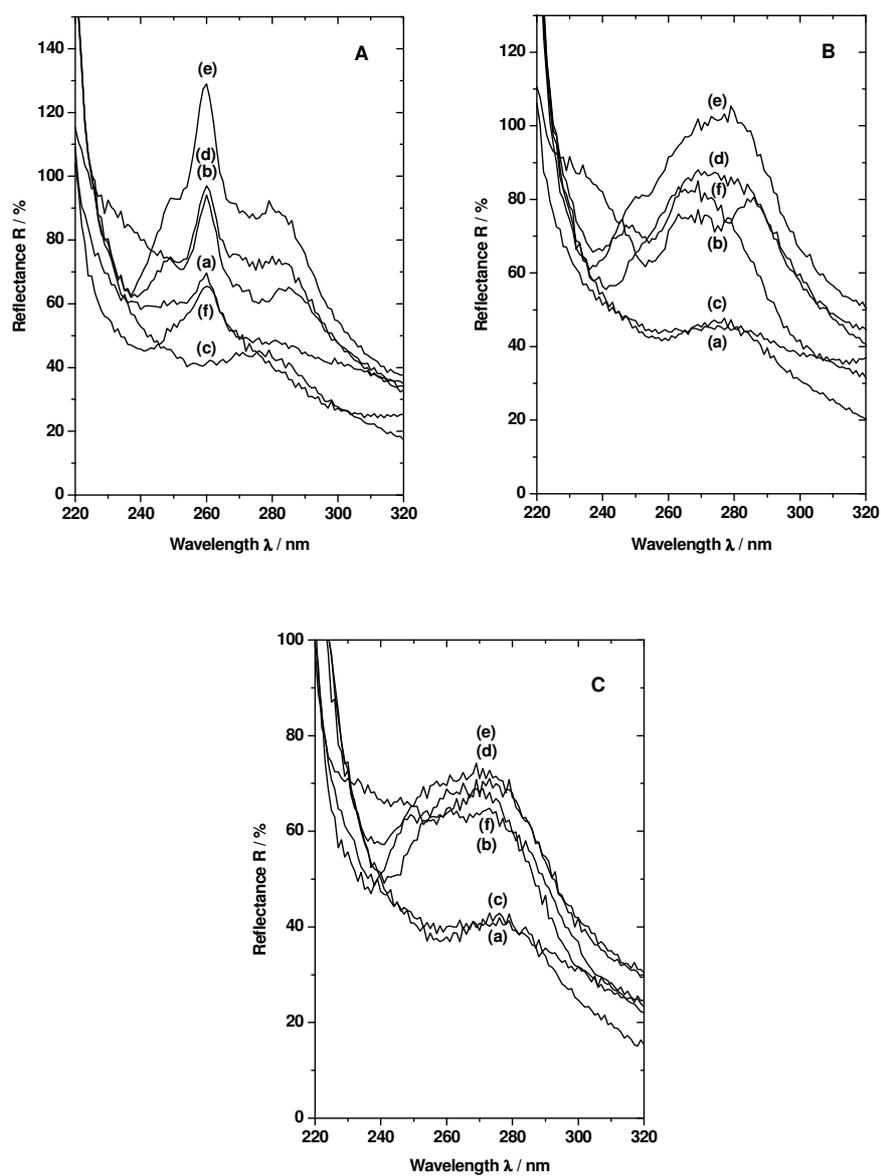
Fig. 7. Reflectance absorption spectra of the grafted chromoionophores: A. 5, B. 6 and C. 7 complexed with transition metal ions and as templates: (a) primary Cu(II) complex, (b) template, (c) Cu(II), (d) Co(II), (e) Ni(II) and Zn(II) complexes with the template.

8   **9**

Fig. 8. Molecular structures of potential fluoroionophores 8 and 9 based on pirene fluorophore group able to be grafted on amino-modified silicate.

In order to bond covalently (graft) the fluoroionophore 8 or 9 to surface of the matrix the prepared mesoporous silica of the type MCM-48 should be functionalized by condensation reaction with APTMS (aminopropyltrimethoxy-silane) (see eqs. 1 and 2).

Complexation of metal ions on the matrix surface functionalized with one of the fluoroionophore was made by immersion and agitation in aqueous solutions of the selected metal salt. By this chemisorption method, complexes of the metal ions were formed with the receptor (ligand) fragments. Selectivity of the recognition material related to Cu(II) was proved by immersing in aqueous solutions of the following metal ion mixtures:

a)   Cu(II), Li(I), Na(I) and K(I),
b)   Cu(II), Mg(II), Ca(II) and Ba(II),
c)   Cu(II), Co(II), Ni(II) and Zn(II).

Concentration of metal ions in the two- and four-component solutions was $2.5 \cdot 10^{-3}$ M for one type of the metal.

Selectivity experiment of the recognition phase chemisorbed in aqueous solutions of the metal ions is illustrated in Figure 9. In the experiment are compared emission spectra of the material after chemisorption of an individual type of the metal ions with the mixture of the analyzed cations; in each series in the mixture are present Cu(II) ions. Thus, in Figure 9 are presented results for alkali (A), alkaline earth (B) and transition metal ions (C) with spectra of Cu(II) as well as the mixture of cations in the series for comparison. Interestingly, in the series with alkaline earth and transition metal ions the emission bands related to Cu(II) and the mixtures of the analyzed cations are overlapped [cf. Fig. 8(A) and (B), spectra (e) and (f)] but in the alkali series the emission spectrum of the cation mixture is lower intensity than the Cu(II) spectrum.

In Figure 10 is shown calibration curve made for the recognition phase chemisorbed with Cu(II) ions in aqueous solution. Dramatical change of the emission intensity measured at band position equal to 400 nm ($\lambda_{exc} = 340$ nm) is present in the Cu(II) concentration range $0.5 - 5.0 \cdot 10^{-3}$ M. At the higher Cu(II) concentration there is observed practically no emission intensity change.
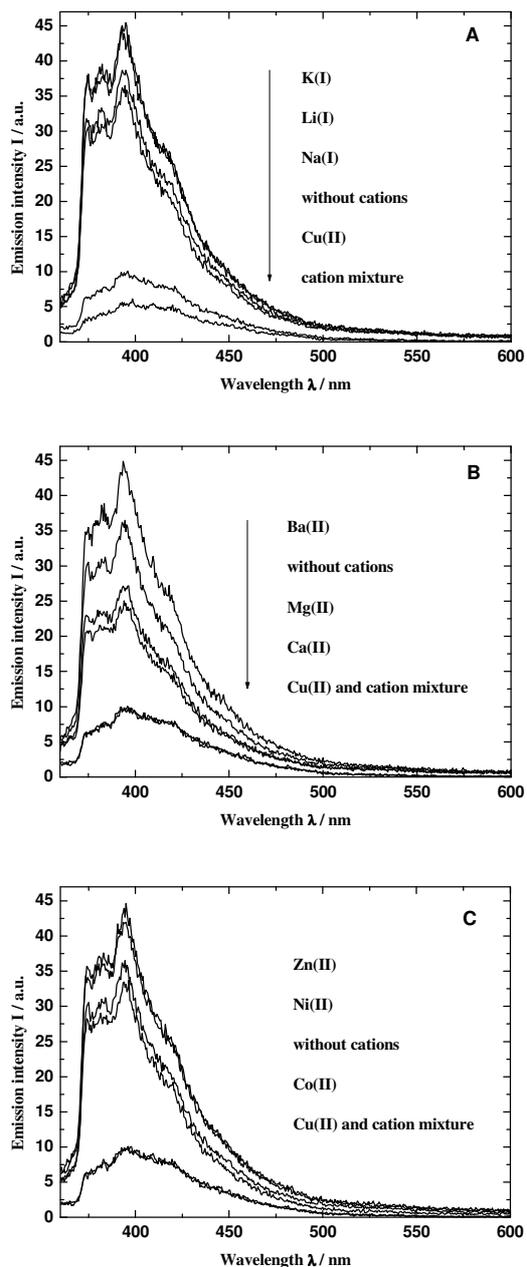
Fig. 9. Fluorescence emission spectra of the recognition phase complexed by cations from aqueous solutions of: A. alkali series and Cu(II), B. alkaline earth series and Cu(II) and C. transition metal series. In the mixtures of cations is present Cu(II).
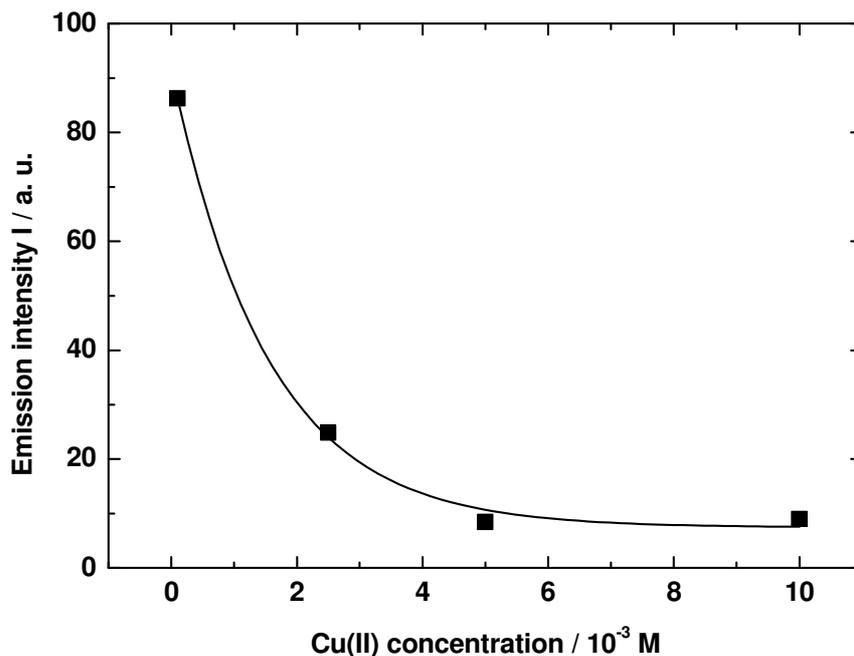
Fig. 10. Calibration curve of the recognition phase for Cu(II) analyte.

3. CONCLUSIONS

- The sol-gel procedure is a versatile method of preparing the optical chemical recognition elements. The recognition elements consist of a matrix or support for the chromionophores and fluoroionophores signalling selectively presence of some metal ions in aqueous solution.

- Materials composed of chromoionophores 1-4 entrapped in silica xerogel matrix at concentration 1.0×10^{-4} mol·g^{-1} silica, treated as optical recognition elements, selectively recognize some metal ions present in aqueous solutions.

- The chromoionophores 1, 3 and 4 incorporated into silica xerogel matrices by the sol-gel procedure are sensitive to Cs^+, Mg^{2+}, Sn^{2+} and Cu^{2+} in aqueous solution in this sense that reflectance absorption spectra specifically changes in the presence of these cations compared with the free ligands or other studied metal ions. This is important for determination of the mentioned

cations in environmental and physiological fluids by UV-Vis spectrophotometry.

- The studied 21-membered chromoionophores (3 and 4) in the recognition elements by their dramatical spectral changes are able to signal when the molar ratio $[Li^+]/[ligand]$ exceeds 1 in aqueous solution.

- Chromoionophores 6 and 7 equipped with two grafting groups can form gate-like templates for Cu(II) ions. This is suggested by similarity of reflection absorption spectra of the primary Cu(II) complex grafted on silicate support and the Cu(II) complex with the template.

- Both the pirene derivatives 8 and 9, as potential fluoroionophores, after covalent attachment on the mesoporous silica matrix, exhibit the most promising properties as components of the recognition elements in the fluorescent chemical sensor for Cu(II) ions.

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CURRICULA VITAE

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