

From metal ions, organic molecules and their complexes to nanostructures in amorphous and vitreous matrices

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This review attempts to present some aspects of glasses and other amorphous materials such as xerogels both from the fundamental and applied viewpoints. Are given three examples of how doped xerogel materials prepared by sol-gel method are emerging as an important means of producing new materials. Moreover, there is present brief description of nanostructural materials.

The first part of this review is devoted to general characteristics of glasses, gels and nanostructures. The second part contains description of such functional materials as oxide glasses, catalyst precursors, chemical recognition phases and luminescent materials.

Thus, firstly oxide glasses are classified by the proximity to the onset of metallization and simultaneously described by their ionic-covalent bond. Secondly, ligand protected metal nanoclusters as immobilized catalysts in oxide xerogels are the point of interest. This type of heterogeneous catalysts are much less investigated than the bare metal particles on supports. The main interest is focused on the function of the ligands.

Then, silica xerogel samples with entrapped series of three fluorescent chemosensors of the *Ant-R-Ant* type, where *Ant* is an anthryl group and *R* is a receptor (spacer) with donor atoms, were prepared as chemical recognition phases. The recognition phase with fluorosensor of the type *Ant-N-O-O-N-Ant*, where N and O are donor atoms, can be regenerated many times and seems to be most promising system for the fluorescent chemical sensor.

Finally, luminescent materials which are based on the antenna effect and are composed of Eu(III) complex (luminescence centre) entrapped in xerogel matrix. In this case results of the experiments concerning the coordination sphere composition show that a cryptand ligand with

aromatic groups and an aromatic co-ligand, settle efficient action the antenna effect and isolate the central ion from each efficient quenchers, as *e.g.* water molecules. In this section is presented influence of nanoparticles of semiconductors of the II-VI type on luminescence properties.

1. INTRODUCTION

Amorphous, meaning *structureless* or *capable of assuming any structure*, describes all solids whose properties do not show a preferential direction, whose rupturing and cracking behaviour is characterized by, for example, the formation of all sorts of random surfaces, often of conchoidal appearance, and in which neither compact nor disperse crystalline components are discernible. Amorphous substances are isotropic, like gases and liquids. Their specification first should be restricted to the statement that they are not crystalline. The methods of X-ray, neutron, and electron diffraction are helpful in distinguishing the so-called *X-ray amorphous* substances from those that are crystalline, and also be used to study the continuous transition between these states. The degree of order present in glasses can be determined by converting the diffraction intensity as a function of angle into a radial pair density distribution function. The equilibrium distance between atoms in chemical bonds results in frequency of corresponding pair distances in amorphous substances being above average, as in crystalline substances, whereas values below the average do not occur in practice. Consequently, certain areas of short-range order usually characterize amorphous substances, like crystalline solids. These often correspond to the structural units of crystalline states, or at least are associated with them through a clear relationship in terms of chemical structure (Figure 1). It may be expected from the orientational character of chemical bonds that the short-range order in the immediate vicinity of any atom also has a successively diminishing effect on the second and third spheres of coordination. It can also be said that there is a quasi-transition to a continuum of pair spacings. A long-range order, as in crystals, does not exist in amorphous substances. The designations *amorphous* and *non-crystalline* describe the same fact and are consequently used as synonyms.

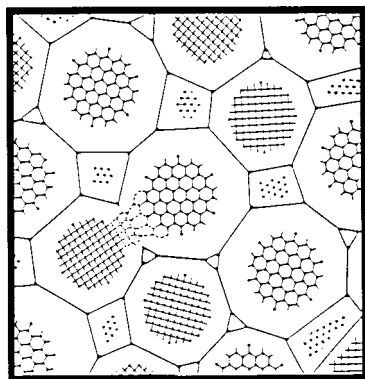


Fig. 1. Diagrammatic section through the bulk structure of silica glass showing clusters of three different polymorphs, indicated by symbolic lattices. Points in the latter represents individual silicon atoms (oxygen atoms are not shown). No lattice is indicated in strained regions, denoting their inability to give coherent diffraction

2. AMORPHOUS MATERIALS

Glasses. Glasses are non-crystalline or amorphous substances. Nevertheless, the term vitreous state is restricted to (i) solids obtained from melts, or (ii) solids produced by other methods and obtained in a compact form. In both cases an essential feature of these materials is that they have a transition temperature region.

Glasses have numerous properties in common with crystalline solids, such as hardness and elasticity of shape.

The opinion expressed in many recent papers is as follows: amorphous substances, irrespective of the method of preparation, ought to be defined as vitreous if they have a transition temperature region, the property typical of glasses [1]. This is not contradictory to the conclusion that the term amorphous solid state has a more comprehensive meaning, broader than that of the vitreous state. It means that all glasses are amorphous, but not all amorphous substances are glasses. For instance, thermally unstable gels can be amorphous, but must not be understood as glasses.

The most popular procedures to obtain glasses are by: (i) sufficiently rapid cooling or quenching of melts or (ii) thermal densification of gels prepared from solutions.

The *sol-gel process* is a chemical synthesis technique for preparing gels and glasses. The method received considerable attention because it possesses a number of desirable characteristics. It enables one to prepare glasses at far lower temperature than is possible by using conventional melting. Compositions that

are difficult to obtain by conventional means because of volatilisation, high melting temperatures or crystallization problems can be produced. In addition, the sol-gel method is a high-purity process, which leads to excellent homogeneity. Finally, the sol-gel approach is adaptable to producing bulk pieces as well as films and fibres.

The brief survey of the characteristic properties of glasses shows them to be intermediate between the ordered crystalline state on the one hand and the essentially disordered, time-dependent structure of liquids on the other. Glasses can be thought of as being liquids with diffusional atomic motion subtracted. Studies of the structure of glasses – although of intrinsic value – gain added importance as an *entrée* into the more difficult studies on liquids. Not only are glasses necessarily more ordered than the corresponding melt, by virtue of a reduction in diffusive motion, vibrational motion is also suppressed as a result of lower measurement temperature. Structural data therefore suffers less thermal broadening [2].

Gels. During the last years it has been widely recognized that the sol-gel process may be used to encapsulate organic and organometallic molecules in an inorganic gel medium. It is now evident that the synthesis of organic-doped gel is not limited to just a few organics. The flexible solution chemistry and the ability to prepare an essentially inorganic matrix with little or no heating means that the sol-gel approach is compatible with a wide variety of organic molecules. The list of organic-doped gels is constantly expanding [3].

The synthesis of materials by the sol-gel process generally involves the use of metal alkoxides, which undergo hydrolysis and polycondensation reactions to give oxide *network colloids* (gels) such as alcogel or hydrogel and then after drying *xerogel*. In the case of these materials it is not possible to make clear distinction between the disperse phase and the dispersion medium. Many gels are examples of the category where both phases consists of interpenetrating networks, the elements of each being of colloidal dimensions [4]. Thus, in porous solids such as xerogels, gas and solid networks interpenetrate.

In our case the sol-gel process can ordinarily be divided into the following steps: forming a solution, gelation and drying [5]. In the preparation of a silica xerogel, we start with an appropriate alkoxide [*e.g.* $\text{Si}(\text{OCH}_3)_4$, tetramethylorthosilicate or TMOS] which is mixed with water and a mutual solvent, such as methanol (MeOH), to form a solution. Hydrolysis leads to the formation of silanol groups $\text{Si}-\text{OH}$. These species are only intermediates as they react further to form siloxane $\text{Si}-\text{O}-\text{Si}$ groups. An example of the formation of a silica gel by the organometallic route is as follows:





In general, the process of hydrolysis and polycondensation are difficult to separate.

The use of the $\equiv\text{Si}-\text{C}\equiv$ bond is a reasonable way to combine organic and inorganic components in a definite manner in the products obtained by the sol-gel procedure [6]. In this way any functional group can be introduced into the inorganic network. In our practice we used such *organically modified silicates* (ormosils) as 3-aminopropylsiloxane $\text{SiO}_{3/2}\cdot(\text{CH}_2)_3\text{NH}_2$ and *N*-(2-aminoethyl)-3-aminopropylsiloxane $\text{SiO}_{3/2}\cdot(\text{CH}_2)_3\text{NH}(\text{CH}_2)_2\text{NH}_2$ [7-11] as well as polydimethylsiloxane $[\text{SiO}_{3/2}\cdot\text{SiO}_{3/2}\cdot(\text{CH}_3)_2]_n$ and 3-glycidoxypropylsiloxane (glymo) $\text{CH}_2\text{CH}(\text{O})\text{CH}_2\text{O}(\text{CH}_2)_3\text{SiO}_{3/2}$ [12, 13].

Nanomaterials. In this paper is used the conventional definition of nanomaterials consisting of particles having characteristic length scale less than about a hundred nanometers. This length is a particle diameter, grain size, layer thickness, or width of a conducting line on an electronic chip [14].

Chemistry plays an important role in creating nanoscale structures, where the modern usage of the term nanostructure implies that control, and often explicit design, of the chemistry (or physics) is required to generate the as-created nanostructure. Two recent review articles summarize the use of chemistry in this small-scale creative effort [15, 16] and use the term nanochemistry to describe synthetic means to nanoscale ends.

Perspectives on nanstructures and nanoscale phenomena need to span the insight and limits of multiple scientific disciplines. Very popular opinion is that the greater benefit of nanostructures would surely be their application in chemistry – particularly in catalysis – only to be countered by the chemist, who also studies nanoscale materials and felt certain that the quantum confinement effects exhibited by nanometer-sized materials would be best expressed in optical or electronic technology where the nanostructure could be isolated from encountering molecules and thereby avoid any risk of chemistry [17].

This exchange highlights another interpretation of the term *nanochemistry* – an interpretation where the questions become: can chemistry be done with (or at) nanostructures; what remains of a nanostructure when it is exposed to molecules with which chemical reaction can occur; can the integrity of a nanostructure – its controlled composition and placement, often laboriously achieved – be assured when it acts as a catalyst to enhance the rate of a chemical reaction – or worse yet, when it acts as a (potentially unplanned) reactant in a chemical reaction; what are the issues when chemical reactions occur at nanostructures or within a nanostructured environment? It is the conceit of this author that these questions need to be acknowledged and thought about in

greater detail than has been to them to date; this discussion is an initial and undoubtedly biased and incomplete attempt to do so.

One place to seek some of the answers to these questions is in the old chemical literature because the chemical preparation of a nanostructure, although bigger than the customary chemical yardstick (a molecule), is nonetheless nothing particularly new. There are different concepts of *customary size* and highlights the relativity of size within scientific disciplines.

The research in such established small domains as colloids, micelles, nucleation phenomena, and supported metal or metal oxide catalysts developed much arsenal now being to design nanochemistry (*i.e.* to synthesize nanomaterials by chemistry [15, 16]) and are stores of both useful information and lessons already learned about nanochemistry (*i.e.* chemical reactions at nanoscale structures). These general concepts include self-organization (*e.g.* self-assembly) and site specificity (*e.g.* templating). What has changed is primarily our current expectations of nanostructures and their properties.

The quest for functional materials prepared by self-assembly has made great progress over the past decade. In this approach, complementary reactivities, geometries and/or physical properties (*e.g.* hydrophobicity) between reaction components direct the assembly from the ‘*bottom up*’ [18]. This strategy is in contrast to the ‘*top down*’ approach taken when components are assembled by directed delivery to specific positions. For instance, Murray and co-workers [19] report an assembly *tour de force* in which both approaches are used. In this work, a macroscopic substrate serves as a template on which nanomaterials self-assemble in a predictable fashion.

Unfortunately, one of the least-discussed aspects of nanotechnology is the requirement to connect the system with to the macroscopic world [20]. Wiring devices to the outside world for power and for input/output is essential for any new material to serve a useful function. Thus, nanotechnology should generally fulfill its two promises, namely devices have to control events at the nanoscale as well as link to the macroscopic world.

3. FUNCTIONAL MATERIALS

Oxide glasses. Herzfeld [21] proposed a criterion for metallicity. He tried to link the metallic state with density and atomic properties. According to this criterion, a solid is metallic when $(R/V_m) > 1$, where R is the molar refractivity and V_m is the molar volume in the condensed state. Duffy [22] found a good correlation for oxides between E_g (energy gap between the valence and conduction bands) and R given by

$$E_g = 20(1 - R/V_m)^2 \quad (1)$$

Bearing in mind this relationship the author has adopted $\sqrt{E_g} = 20(1 - R/V_m)$ as a measure of how near an oxide is to the onset of metallization.

For traditional oxide glasses, often the principle of acid-base chemistry can be successfully applied. However, nowadays the attention is focused on electro/optical/magnetic properties of glasses. It has been some years ago made an attempt by Duffy [22] to systematize the chemical and physical properties of component oxides with the properties of the final material.

It is convenient to use Duffy's method for charting the proximity of the studied oxide glass to the onset of metallization, but instead of the oxygen electronegativity, x_o (*cf.* ref. 22) we adopted the molar refractivity of oxide ions, $R_{O^{2-}}$, to characterize ionic/covalent bond characteristics. Since oxides can approach the non-metal – metal transition whether they are essentially covalent or essentially ionic, a sensible presentation would be to use a horizontal line for covalent/ionic scale and the vertical to present a growing tendency for the onset of metallization (see Figure 1).

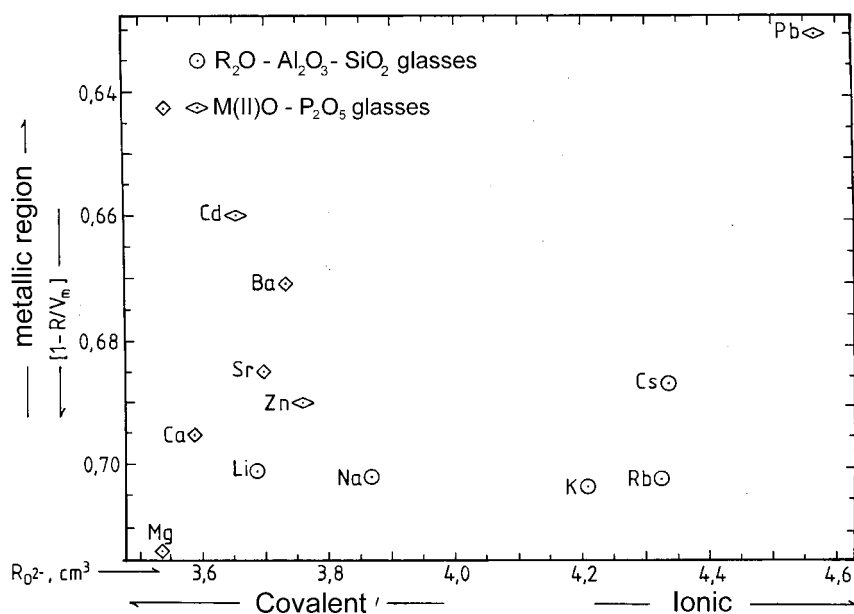


Fig. 2. Chart of oxide glasses. Covalent glasses are to the left and ionic glasses are to the right-hand. The height above the covalent-ionic line represents the proximity to the non-metal/metal transition (*cf.* ref. 22)

The binary and ternary oxide glasses are charted in Figure 6. For these systems the classification shows an average character of the bond to oxygen in the material. It is seen how the phosphate glasses with Mg and Ca [24, 25] are toward the covalent side, while the PbO-P₂O₅ [24, 26] and aluminosilicate

systems with Cs and Rb [27] are to the ionic side. Due to the glass composition the bond to oxygen in the lead phosphate is higher ionic than in the caesium aluminosilicate glass, in spite of Cs-O bonding is more ionic than Pb-O in the pure oxides.

All the glasses as products of the reaction between acidic and basic oxides are colourless insulators [23]. Thus, they are far below the horizontal line drawn for $(1 - R/V_m) = 0.38$, above this value pure oxides are expected to be intensively coloured, and also below another division line $[(1 - R/V_m) = 0.45]$ which separates semiconducting and insulating oxides (*cf.* ref. 22).

Heterogeneous catalyst precursors. Polymer-supported metal complex catalysts are currently a field in which research is particularly active [28]. In the case of oxidation reactions, these catalysts include thermo-oxidatively stable supports such as hybrid organic-inorganic polymers prepared by the sol-gel method [29]. In this way any functional group can be introduced into the inorganic network [6-11, 30, 31]. In our case these groups are mono- or bidentate ligands like $-(\text{CH}_2)_3\text{NH}_2$ or $-(\text{CH}_2)_3\text{NH}(\text{CH}_2)_2\text{NH}_2$, respectively, for transition metal ions. These ions create coordination cross-linking points with the amino groups in the organically modified silicate xerogels.

A network consisting of $\text{SiO}_{4/2}$ content in the xerogels enables control over the concentration of transition metal complexes to be maintained at the same time. This should result in an increased distance between the metal complexes and in a reduction in the number of nitrogen atoms in the coordination sphere. The transition metal ion is characterised by its ability to form a wide variety of coordination complexes in which octahedron is predominant.

Organically and coordinatively modified oxide xerogels can be used as catalyst precursors. In the preparation procedure it is important to change the coordination environment of the central ion, *i.e.* its composition and symmetry [32]. Our papers describe our most recent synthesis, as well as the coordination state and thermal properties of the two series of aminated materials complexed with copper(II) [11], nickel(II) and cobalt(II) [31] ions.

Because the xerogel materials are considered to be catalyst precursors, our studies were focused on their coordination and thermal properties. The prepared xerogels, such as silica, aminated silicates with $N = -(\text{CH}_2)_3\text{NH}_2\text{SiO}_{3/2}$ and $N-N = -(\text{CH}_2)_3\text{NH}(\text{CH}_2)_2\text{NH}_2\text{SiO}_{3/2}$, as well as those entities complexed with Cu(II), were characterised by FT-IR spectroscopy. During gelation and thermal decomposition the materials were analysed EPR spectroscopy. The xerogels were additionally studied by UV-Vis absorption spectroscopy and the gaseous products of the thermal decomposition of these materials in Ar atmosphere were investigated by the use of FT-IR spectroscopy coupled with TG and DTG thermal analysis. These data were complemented by

temperature-programmed decomposition (TPDec) in a 2% O₂ = 98% Ar stream coupled with quadrupole mass spectroscopy [11].

We may conclude that the coordination of the Cu(II) complexes with the *N* and *N-N* ligands undergoes changes during the sol-gel process (gelation), as follows:

- (1) In xerogel of the type [CuN_{*n*}(NO₃)₂]·N_{5-*n*}·5*x*SiO_{4/2} coordination forms are present with *n* ≤ 4. However, in N xerogels poor in amino groups, e.g. as when *x* = 80, only the form termed **a2** with *n* = 1 exists (Figure 2A).
- (2) Owing to the chelate effect, the xerogel [CuN-*N_n*(NO₃)₂]·N-*N_{2-n}*·2*x*SiO_{4/2} exhibits two coordination species: **aa1** (*n* = 2), present also prior to gelation, and **aa2** (*n* = 1), as shown in Figure 2B.

During thermal decomposition of the aminated xerogels, amino groups such as H₂N(CH₂)₃ and H₂N(CH₂)₂·HN(CH₂)₃, which participate in the coordination sphere of Cu(II), are removed from the xerogels at lower temperatures than the entities trapped in gel network outside the coordination environment. Therefore, at temperatures above 250 °C (e.g. 400 °C) the coordination form **t** with Cu(II) ion in an oxygen environment exists in the decomposed xerogels (Figure 2C).

Recognition phases of optical sensors. In general, a chemical optical sensor consists of a *chemical recognition phase* coupled with a transduction element. Although a variety of interactions can be used as the basis for chemical recognition phase, a selective binding or complexation reaction is most commonly used. The extent to which the analyte interacts with the chemical recognition phase determines the magnitude of the signal. Typically, the measured signal is related to the concentration (activity) of the analyte through a previously prepared calibration curve.

Optical fibre technology is usually used to transmit electromagnetic radiation to and from a sensing region that is in direct contact with the sample. In one sample design, a chemical recognition phase is used to generate an analyte-dependent, spectroscopically detectable signal within the sensing region of the fibre. The chemical changes that occur due to interactions between the analyte and the immobilised reagents are measured spectroscopically by analysing the radiation that returns from the sensing region [33]. A molecule that signals the presence of an analyte is called *chemosensor* [34].

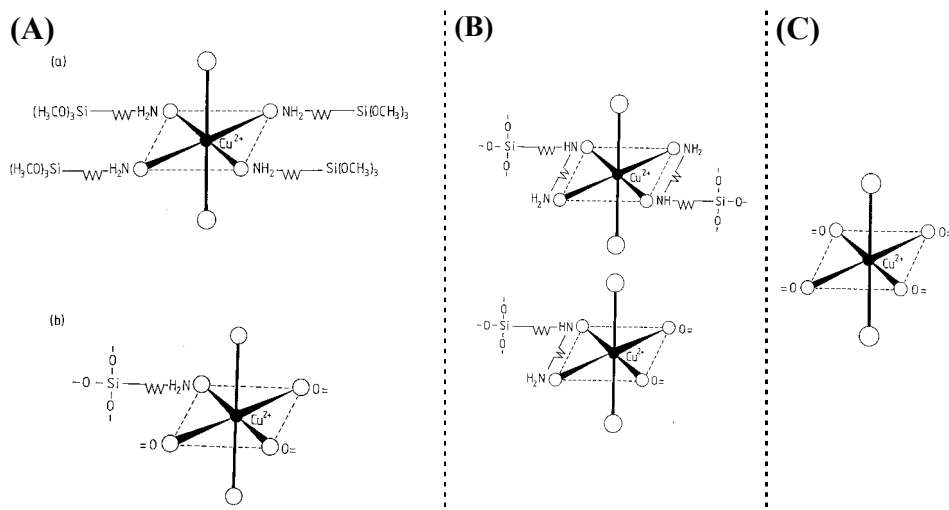


Fig. 3. Proposed structures of the coordination sphere of Cu(II) complexed with **(A)**. *N* ligand (a) coordination form **a1**; (b) coordination form **a2**; **(B)**. *N-N* ligand (a) coordination form **aa1**; (b) coordination form **aa2**. **(C)**. Coordination form **t** present in silica and *N* (or *N-N*) xerogels after thermal decomposition decomposed at above 250 °C. After ref. 9

Fluorescence is particularly well suited for optical sensing because emitted light returning from the chemosensor part of a molecular device with many functions (*i.e.* supramolecular system) can easily be distinguished from the excitation light. Owing to the sensitivity of fluorescence even low fluorophore levels can be detected. Very oft fluorescence sensing is based on intensity measurements because of their simple instrumentation.

The photonic signalling of a host-guest recognition event in a chemosensor can be easily arranged by coupling a receptor to a lumophore. However, the supramolecular nature of the system can be best preserved by interposing a spacer between the original units. Then, the components or modules, each with its characteristic attributes, are clearly recognisable. If the components were completely isolated, the system would be unable to transduce the guest recognition event into a photonic signal. Hence is needed a lumophore-receptor (ligand) interaction which can transcend the spacer.

Besides it is interest in photochemistry, *photoinduced electron (or energy) transfer* (PET) from a donor atom in a conjugate chemosensor is a process largely used in the design of fluorescent ion sensing molecules. One of the simplest systems is based on fluorescent aromatic compounds linked to amino groups and proposed as possible fluorescent proton or metal sensors [35]. In this case, the fluorescence of the fluorophore “lights on” when the amino groups is

coordinatively bonded. In the absence of metal ions, the fluorescence is quenched by a PET originated from the nitrogen lone pair (Figure 3).

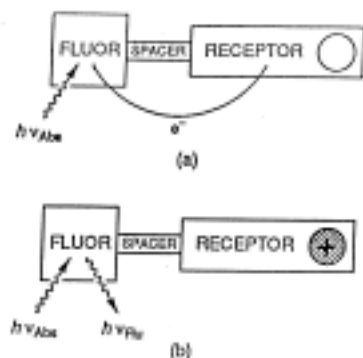


Fig. 4. Schematic representation of photoinduced process in a 'fluorophore-spacer-receptor' signalling system: a) when cation-free, b) when cation-bound [36]

In our papers [37-41], we discuss experiments with chemical recognition phases consisting of the prepared fluorosensors such as bis-9-anthryl quadridentate derivatives (shown in Figure 4) immobilised in porous silica xerogel.

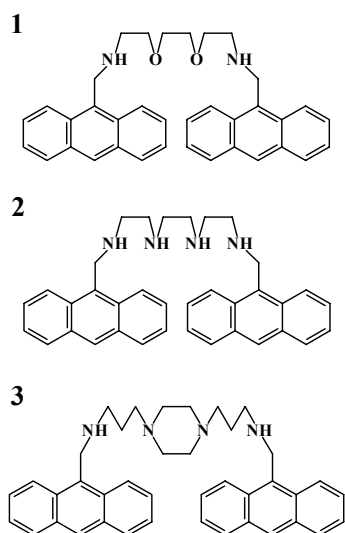


Fig. 5. Molecular structures of the bis-9-anthryl derivatives of the type Ant-R-Ant, where R is a quadridentate receptor

The results show that the supramolecular system **1** of the type Ant-N-O-O-N-Ant, where Ant is anthryl group and N or O is donor atom in the receptor (ligating) group, is the most useful as a fluorosensor (Figure 5). Thus, among the studied chemosensors the molecular system **1** is the most promising as a component of the recognition phase in the fluorescent chemical sensor for Cu(II) ions in presence of other transition metal ions [*e.g.* Co(II), Ni(II) and Zn(II)].

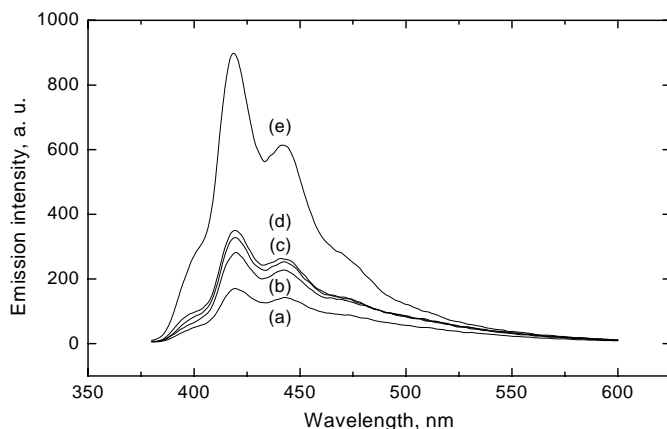


Fig. 6. Fluorescence emission spectra of the fluorosensor **1**: a) uncomplexed and complexed with: b) Co(II), c) Ni(II), d) Zn(II) and e) Cu(II) ions [39]

The chemical recognition phase with **1** undergoes cycles chemisorption (complexation)-desorption (decomplexation). The plot in Figure 7 testifies that, after chemisorption and desorption of Cu(II) in the recognition phase, there is in each step a distinct difference between the high emission intensity for the complexed material and the low intensity for the desorbed one. The observed rising trend of the fluorescence intensity indicates that such high bis-9-anthryl dopant concentration as $2.5 \cdot 10^{-5}$ mole g^{-1} SiO_2 can cause concentration quenching. In this way, fluorescence intensity could increase after each step as a result of the fluorescence species being leached from the silica matrix [41].

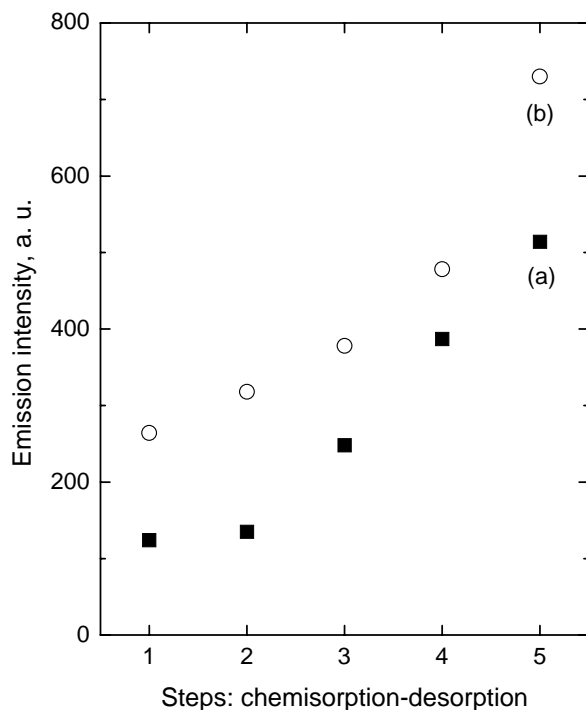


Fig. 7. Fluorescence intensity changes recorded at 412 nm during five steps: (a) chemisorption of Cu(II) from aqueous solution – (b) desorption by protonation [41]

We are interested also in the chemical recognition phase which consists of silica xerogel (as a matrix) and the supramolecular dopants of the type $A3nCn-CH_2-bpy$, where $n = 4, 5$ and 6 [42]. The dopant as a chemosensor contains two coordinatively active subunits (receptors), namely 2,2'-bipyridine (bpy) and aza-3n-crown-n ($A3nCn$) groups (Figure 6), while the aromatic segment plays a fluorophore role. The subunits are connected with CH_2 group.

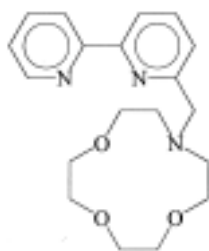


Fig. 8. Molecular structure of $A3Cn-CH_2-bpy$ chemosensor, where $n = 4$

The room temperature fluorescence spectra of the free fluorosensors in silica and the complexed ones with representative Cu(II) and V(II)O ions are shown in Figure 7. Quenching of fluorescence for the complexed species is observed. It means that they act in reversed PET logic as compared with bis-9-anthryl derivatives mentioned above. The quenching effect is especially great in the case of the Cu(II) complex with A12C4-CH₂-bpy fluorosensor as compared with the fluorescence intensity of the respective free entities immobilised in silica [*cf.* in Figure 7(a)]. The fluorosensors complexed with Cu(II) cations in each case exhibit near zero emission intensity, whereas vanadyl cation in this situation possesses an intermediate position among the transition metal ions studied [42].

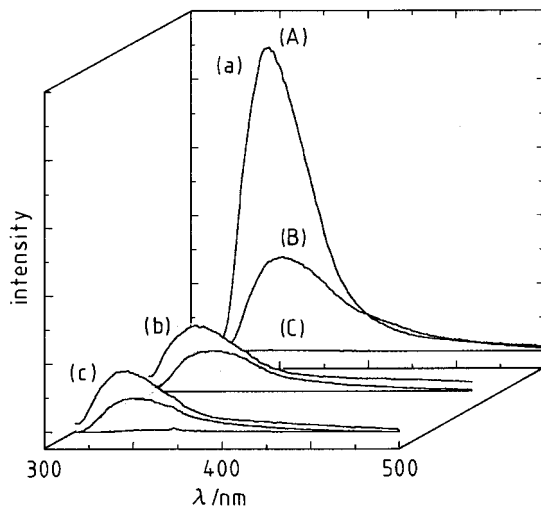


Fig. 9. Fluorescence quenching effect due to the coordination of metal ions in silica xerogel doped with A3Cn-CH₂-bpy: (a) n = 4; (b) n = 5; (c) n = 6. Fluorosensors uncomplexed (A), and complexed with (B) V(II)O and (C) Cu(II) [41]

Luminescent materials. Materials containing lanthanide ions have been used as phosphors and laser materials because of their sharp, intensely luminescent *f-f* electronic transitions. In particular, a number of lanthanide complexes showed a bright and narrow lanthanide ion emission. These emissions usually resulted from the so called "antenna effect", which is defined as a light conversion process *via* an absorption-energy transfer-emission sequence involving distinct absorbing by a ligand (light collector) and emitting by a metal ion. In such a process, the quantities that contribute to the luminescence intensity are: (i) the intensity of the ligand absorption, (ii) the efficiency of the ligand-to-metal energy transfer, and (iii) the efficiency of the metal

luminescence (Figure 1). This phenomenon has been reviewed by Sabbatini et al. [43].

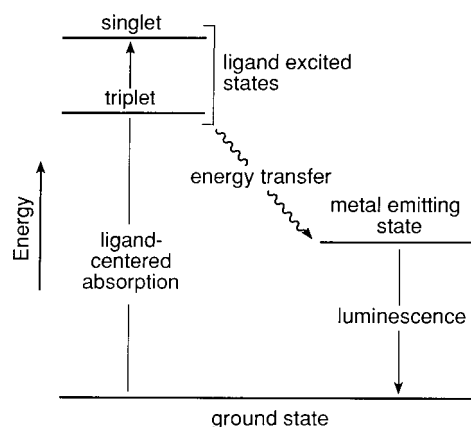


Fig. 10. Schematic representation of the antenna effect involving absorbing ligand and emitting metal subunits [43]

In order to increase the intensity of the lanthanide luminescence exploiting the antenna effect, complexes with strongly absorbing cryptands have been designed, *e.g.* cryptands with aromatic segments, *e.g.* 2,2'-bipyridine (*bpy*), 1,10-phenantroline (*phen*) or 3,3'-biisoquinoline (*biq*), which show intense absorption bands in the UV region due to π - π^* transitions.

According to the theory of non-radiative transitions in lanthanide complexes [44-46], the non-radiative relaxation between various J states may occur by interaction of the electronic levels of the lanthanide ion with suitable vibrational modes of the environment. The efficiency of these processes depends on the energy gap between the ground and excited states and the vibrational energy of the oscillators [44, 45, 47]. When solvents containing O-H groups are coordinated to lanthanide ions, efficient non-radiative deactivations take place *via* vibronic coupling with the vibrational states of the O-H oscillators [48, 49, 13]. If the O-H oscillators are replaced by the low frequency O-D oscillators, the vibronic deactivation pathway becomes much less efficient.

In attempt to improve the luminescence properties of Eu(III) cryptates, the *bpy* or *biq* units of cryptands were replaced with *bpyO*₂ or *biqO*₂ [50]. Results on the luminescence of Eu(III) complexes with the dioxide derivatives have shown that the included central metal ion is better protected from interactions with water than in the case of the [Eu(*bpy* derivative)]³⁺ or [Eu(*biq* derivative)]³⁺ cryptate and that these complexes present a significant gain in light-conversion efficiency over earlier europium cryptates.

In order to reduce the non-radiative decay from the excited state of Eu(III) we tried to eliminate O-H oscillators in the short range, *i.e.* in the coordination

environment of the central ion and in the long range, *i.e.* in the xerogel matrix. To realize the short-range approach we have tested several ligands for Eu(III) ion luminescence characteristics [12]. Among the ligands used, the best results (*i.e.* the higher emission intensity and longer lifetime) shows the [*biqO*₂.2.2] cryptand, where *biqO*₂ is 3,3'-biisoquinoline-2,2'-dioxide (Figure 11A, structure 1).

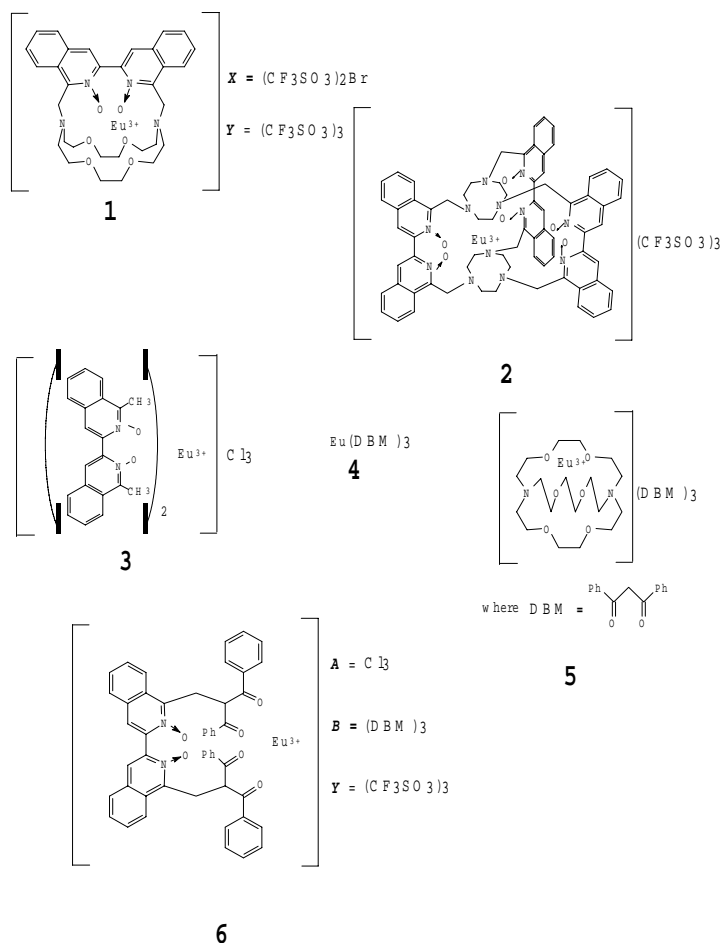


Fig. 11A. Molecular structures of the studied: Eu(III) complexes (cryptates)

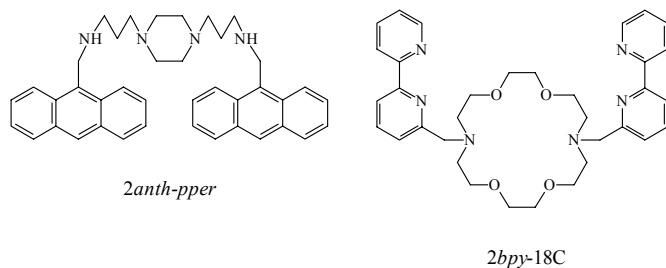


Fig. 11B. Molecular structures of the studied: some co-ligands

Luminescence intensity can be increased if the coordination sphere is completed additionally with co-ligands such as *1,10*-phenanthroline (*phen*), *2,2'*-bipyridine (*bpy*), triphenylphosphine oxide (*TPPO*) [12, 51] or other aromatic systems replacing water molecules from the first coordination sphere of Eu(III) (in Figure 11B).

To eliminate the O-H quenchers in the long range of Eu(III) surrounding we used D₂O instead of H₂O as a reagent and deuterated methanol (MeOD) instead of MeOH as a solvent in the sol-gel procedure [12]. Good results can be also obtained if the Eu(III) cryptate is encapsulated in methyl-modified silicate xerogel dried by means of (Me₃Si)₂NH agent and additionally at elevated temperature [51].

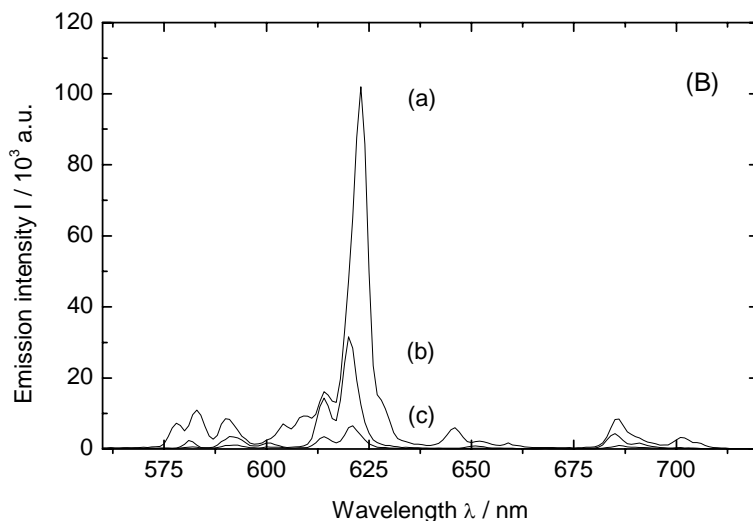


Fig. 12. Luminescence emission spectra of **1X** cryptate entrapped in matrices: (a) TiO₂-Glymo (1:1), $\lambda_{\text{exc}} = 352$ nm; (b) SiO₂-Glymo (1:1), $\lambda_{\text{exc}} = 361$ nm; and (c) ZrO₂-Glymo (1:1), $\lambda_{\text{exc}} = 354$ nm [13]

Thus, to improve luminescence properties, *i.e.* to enhance the emission intensity and lengthen the lifetime of the Eu(III) excited state in the materials, we recently analyse influence of ligands, co-ligands, anions and matrix materials on the Eu(III) luminescence characteristics in its complexes (cryptates). Such components of the matrix materials as oxide mixtures (titania-silica and zirconia-silica), polydimethylsiloxane (*PDMS*) as well as 3-glycidoxypropyl (Glymo)-modified oxide strongly influence on the luminescence activity (Figure 12) [13].

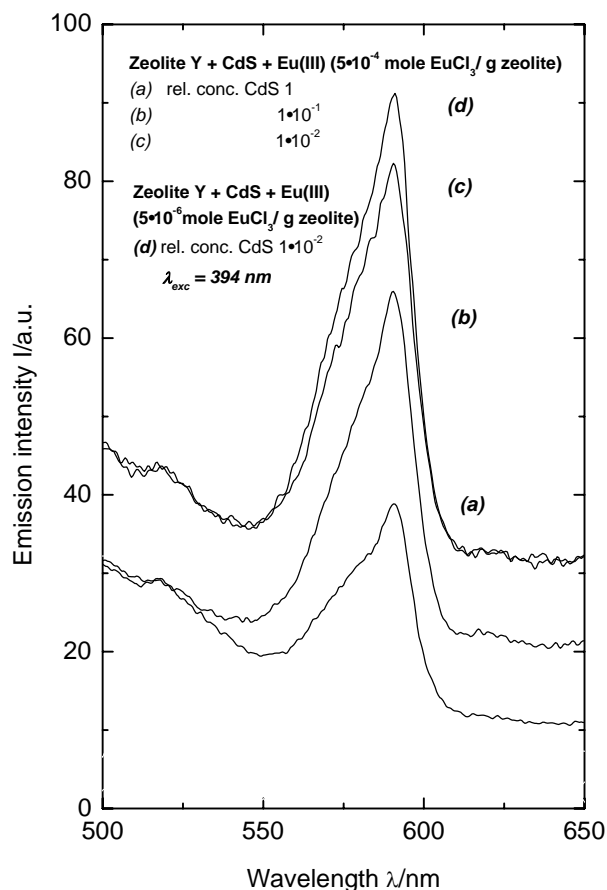


Fig. 13. Emission spectra of semiconducting ZnS nanoparticles activated with Eu(III) ions entrapped in zeolite Y

In general, Eu(III) ion should be isolated particularly from effectively quenching O-H groups. On the other hand, O-H oscillators can be eliminated from the materials by a chemical agent and/or by drying in elevated temperature. Finally, the prepared materials with the Eu(III) cryptate were tested after exposure to UV radiation during a time period. Namely, there is

problem related to photodegradation of the organic antenna system in a luminescent material during excitation by high-energy quanta [52].

It is now evident that in such multiply systems as the luminescent materials with Eu(III) complexes prepared by the sol-gel procedure, efficiency of their luminescence depends first of all on presence of quenching O-H oscillators not only in the shortest distance from the central ion (first coordination sphere), but also in the long distance, *i.e.* in matrix.

A considerable effort has been spent in the preparation and investigation of the family of II-VI nanoscale semiconductors due to their fundamental optical properties [53-55]. We prepared nanocrystals of CdS with very narrow size distribution in zeolite Y with. Luminescence action of these materials doped with Eu(III) complexes shown in Figure 13 is characteristic for monodisperse CdS nanoparticles [56].

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