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LUMINESCENT MATERIALS, RECOGNITION PHASES OF THE CHEMICAL SENSORS AND HETEROGENEOUS CATALYSTS PREPARED BY SOL-GEL METHOD

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Abstract
The sol-gel process enables one to prepare oxide xerogels at room temperature. By using this method, it is possible to encapsulate a wide variety of organic, complex (organometallic) molecules and metallic nanoparticles stabilized by organic ligands in the inorganic or inorganic/organic hybrid matrix. Studies of this new type of inorganic/organic composite have evolved towards the deliberate doping of the supramolecular species. This review gives three examples of how doped xerogel materials prepared by the sol-gel method are emerging as an important means of producing new materials. The first part of this review is devoted to 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. Secondly, 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. In the third part of this paper, ligand protected metal nanoclusters as immobilized catalysts 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.

Keywords: sol-gel, xerogel, ligand, organometallic

1. Introduction

The synthesis of materials by the sol-gel process generally involves the use of metal alkoxides or organical derivatives of these alkoxides which undergo hydrolysis and condensation polymerisation reactions to give alcogel and then xerogel after drying. The synthesis of oxides and organically modified oxides by this approach has been a subject of several books and reviews [1–4].

The method has received considerable attention because it possesses a number of desiderable characteristics. It enables one to prepare glasses at far lower temperatures than is possible by using conventional melting. Compositions which 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.

During the past ten years it has been widely recognized that the sol-gel process may be used to encapsulate organic and organometallic molecules as well as metallic nanoclusters in an inorganic or inorganic/organic hybrid medium. It is now evident that the synthesis of this types of xerogels is not limited to just a few substances. The flexible solution chemistry and the ability to prepare a matrix with little or no heating means that the sol-gel approach is compatible especially with a wide variety of organic molecules. In general, the list of dopants in this case is constantly expanding [5].

Prior to the sol-gel work, the incorporation of organic, organometallic and metallic species in solids generally was restricted to the use of frozen solvents or organic polymer matrices. The present approach represents a totally new type of inorganic/organic composite material because the oxide skeleton not only offers a significantly more ionic environment but also is thermally, chemically and dimensionally more stable. Thus, studies of organic, organometallic or metallic doped xerogels have began to develop substantial breadth; from investigations of doped xerogels for luminescent materials, to the development of recognition phases of optical chemical sensors and heterogeneous catalysts.

2. 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 (see Fig. 1).

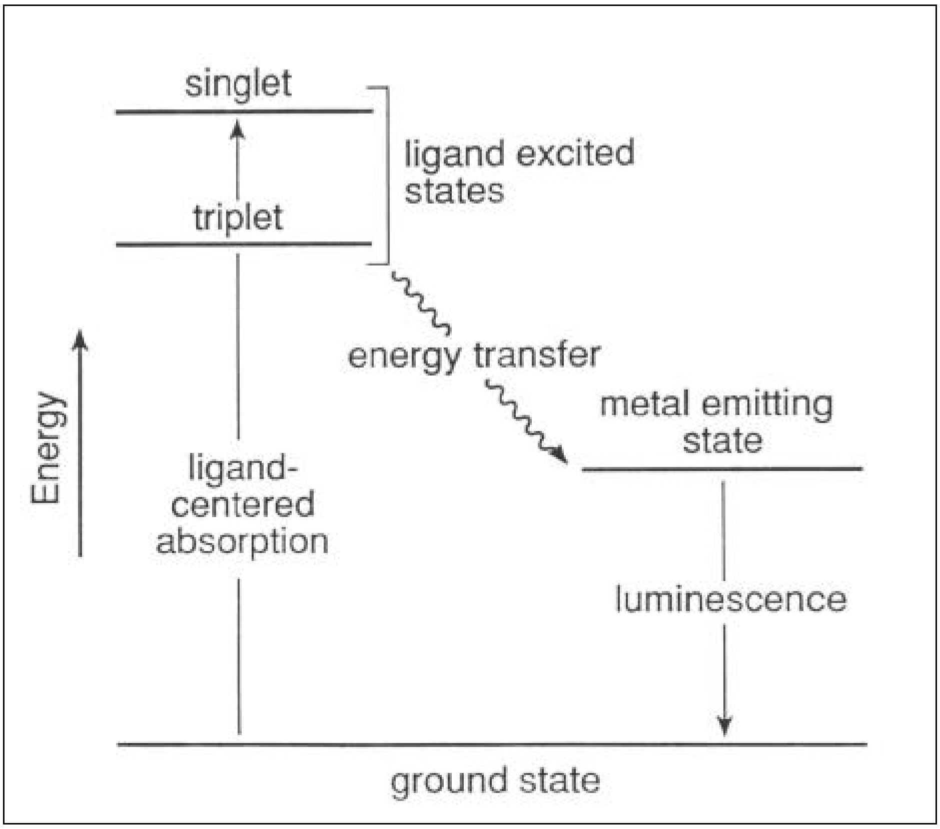

Fig. 1. Schematic representation of the antenna effect involving absorbing ligand and emitting metal subunits [6].

This phenomenon has been reviewed by Sabbatini et al. [6]. The luminescence properties of lanthanide complexes in a variety of solutions have extensively been investigated [7–11] which demonstrated that lanthanide complexes have superior fluorescence properties with respect to simple salts in solutions. However, conventional ligands are not able to give rise to inert complexes, especially in aqueous solution where solvent molecules efficiently compete to occupy coordination sites. In fact, the cryptand ligands possess spheroidal cavities and donors atoms, like oxygen and nitrogen. This type of ligands makes high stable complexes with lanthanide ions and is able to shield the encapsulated ion from interaction with surrounding.

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-phenatroline (phen) or 3,3'-biisoquinoline (biq), which show intense absorption bands in the UV region due to π–π* transitions.

In attempt to improve the luminescence properties of Eu(III) cryptates, the bpy or biq units of cryptands were replaced with $bpyO_2$ or $biqO_2$ [12]. 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 $[Eu \subset bpy\ derivative]^{3+}$ or $[Eu \subset biq\ derivative]^{3+}$ cryptate and that these complexes present a significant gain in light-conversion efficiency over earlier europium cryptates.

The sol-gel process is a potentially attractive means of synthesizing novel luminescent materials. The incorporation of lanthanide complexes, particularly europium(III) complexes has been investigated in details [13–20]. Xerogels doped with Eu(III) complexes have shown substantially improved luminescence characteristics with respect to comparable materials containing simple metal.

According to the theory of non-radiative transitions in lanthanide complexes [21–23], 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 [21, 22, 24]. 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 [25–27]. If the O-H oscillators are replaced by the low frequency O–D oscillators, the vibronic deactivation pathway becomes much less efficient.

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 [19]. Among the ligands used, the best results (*i.e.* the higher emission intensity and longer lifetime) shows the [*biq*O_2.2.2] cryptand, where *biq*O_2 is *3,3'*-biisoquinoline–*2,2'*-dioxide (Fig. 2A, structure **1**).

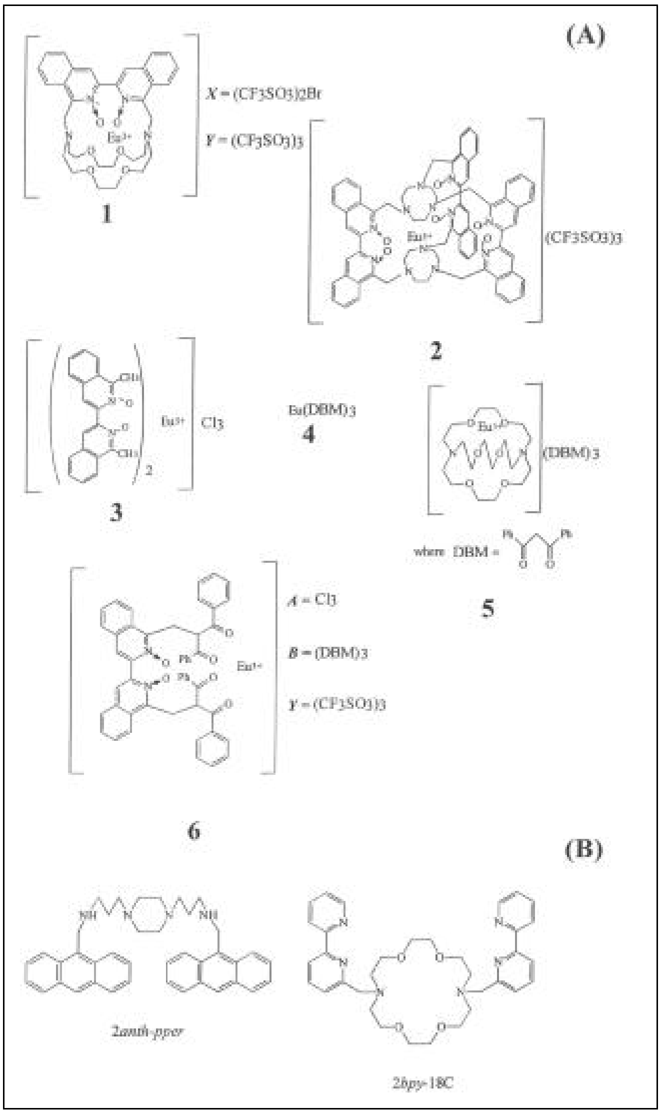

Fig. 2. Molecular structures of the studied: (A) Eu(III) complexes (cryptates) and (B) some co-ligands.

Luminescence intensity can be increased if the coordination sphere is completed additionally with co-ligands such as *1,*10-phenantroline (*phen*), *2,2'*-bipyridine (*bpy*), triphenylphosphine oxide (*TPPO*) [19, 20] or other aromatic systems replacing water molecules from the first coordination sphere of Eu(III) (in Fig. 2B). To eliminate the O–H quenchers in the long range of Eu(III) surrounding we used D_2O instead of H_2O as a reagent and deuterated methanol (MeOD) instead of MeOH as a solvent in the sol-gel procedure – cf. in Tab. 1 [19].

Tab. 1. Preparation procedure and its influence on the relative luminescence intensity I_{rel} in the band maximum and luminescence lifetime *t* of the cryptate 1 immobilized in $[SiO_{4/2} + Si(CH_3)_2O_{2/2}]$ xerogel.

Reagents	Solvent	Catalyst	Relative intensity (I_{rel})[a]	Lifetime t / µs [b]
$Si(OCH_3)_4+H_2O$	CH_3OH	Acetic acid	0.36	574
$Si(OCH_3)_4+D_2O$	CH_3OH	Acetic acid	0.40	587
$Si(OCH_3)_4+D_2O$	CH_3OD	Acetic acid	1.0	608

[a] $\lambda_{exc} = 352$ nm, $\lambda_{em} = 622.6$ nm

[b] $\lambda_{exc} = 394$ nm, $\lambda_{em} = 615.0$ nm

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 (Fig. 3) [20].

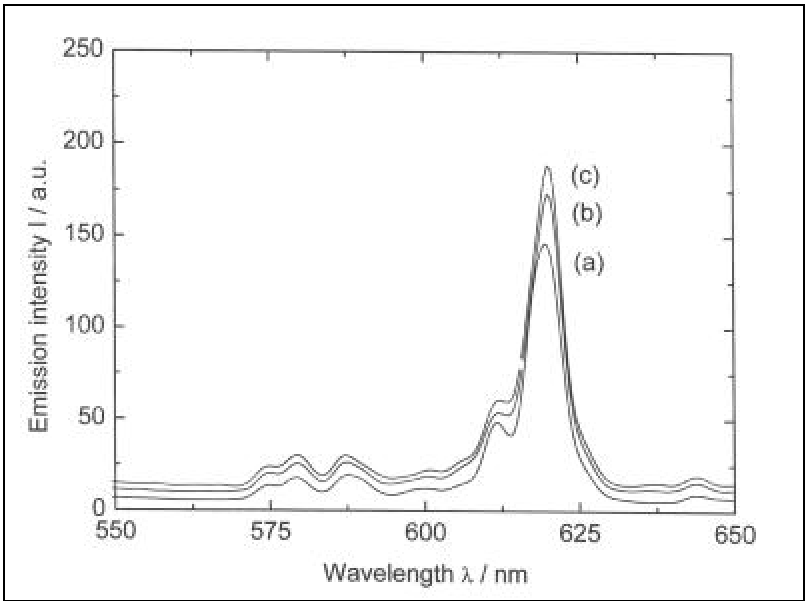

Fig. 3. Emission spectra of material prepared by entrapment of cryptate salt 1X in methyl modified silicate matrix: (a) dried at room temperature, (b) after reaction with (Me3Si)2NH reagent and (c) after the reaction as previously and drying at 80oC. λexc = 3 [27]

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, coligands, 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), polidimethylsiloxane (PDMS) as well as 3-glycidoxypropyl-modified oxide strongly influence on the luminescence activity. 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 [28].

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.

3. Recognition phases of the fluorescent chemical sensor

Luminescence is perhaps the most convenient and an easily detectable property which can be used to signal the occurrence of molecular events in real time and in real space. Owing to fluorescence, it can be unambiguously detected even at very low concentrations and can be switched on and off (enhanced/quenched) through well-defined mechanisms, namely electron transfer or energy transfer [29].

Luminescent molecular receptors capable of sensing a variety of analytes (H^+ [30], *s*- and *d*-block metal ions [31, 32], anions [33] and amino acids [34]) have been developed. Most of them have been designed by following a two-component approach, *i.e.* by covalently linking a receptor subunit displaying selective affinity towards the envisaged substrate to luminescent fragment (*fluorophore*) [35]. The sensing compounds incorporating a binding site, a fluorophore, and a mechanism for communication between the two are called *fluorescent chemosensors* (*fluorosensors*) [30, 36–40].

Recently, many investigations have been done on chelation-enhanced fluorescence [41] to make fluorosensors. In all these systems [35, 42], complexation by non-transition-metal ions or protonation of the amino groups present enhances the fluorescence quantum yield, as fluorescence quenching due to *photoinduced electron transfer* (PET) in the receptor molecule will no longer be operative. Transition-metal-based molecular fluorescent signalling systems are eagerly awaited [30, 39, 40, 43]. These systems would be useful not only at real-time and real-space monitoring devices in biology but also as versatile molecular switching devices. Transition metal ions are known as effective fluorescence quenchers [44–46]. We present here the very rear systems [41] where transition metal ions Cu(II) and Ni(II), along with Co(II) and Zn(II) ions, cause enhancement of fluorescence. The signalling possibilities arise from the fact that the fluorophore-spacer-receptor system in the cation-free situation has been chosen such that its fluorescence is switched off by the PET process, as in Fig. 4 [47, 48].

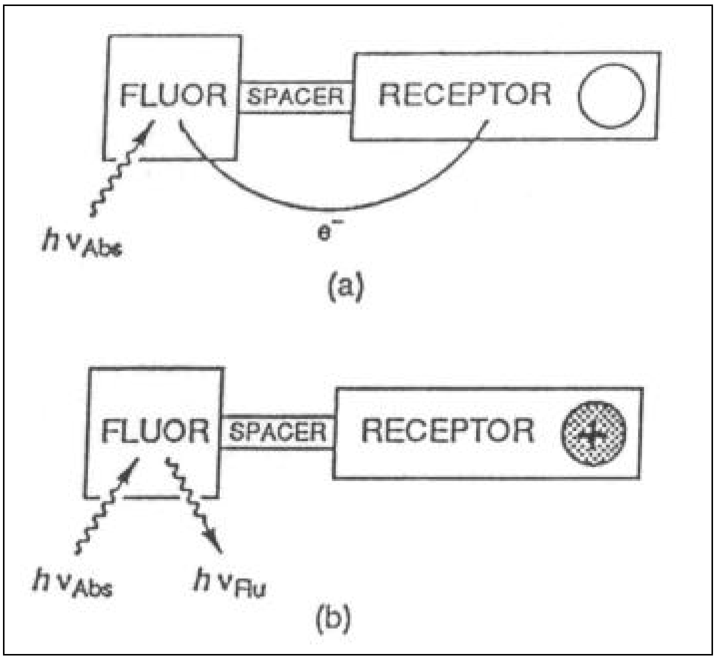

Fig. 4. Schematic representation of photoinduced processes in a 'fluor-spacer-receptor' signalling system (a) when cation-free and (b) when cation-bound.

The PET process, in turn, can be suppressed by the entry of a cation into receptor by the cation-induced increase of the ionisation/oxidation potential of the receptor. At the simplest level this is an electric field effect. However, other ways of inhibiting electron transfer are available such as these three approaches: conformational changes, local polarity modulations, and hydrogen bonding. Such a suppression of the PET process means that fluorescence becomes the dominant decay channel of the excited fluorophore [30]. Thus, cation entry is signalling by photon output when interrogated by excitation photons.

The fluorophore and the receptor units can be connected covalently or non-covalently. In the simplest covalently linked fluorophore-receptor systems, a $-(CH_2)_n-$ bridge may suffice to keep the two subunits together. However, the features of the spacer are not irrelevant, as they affect the signal transduction mechanism and, ultimately, determine signalling efficiency (Fig. 5).

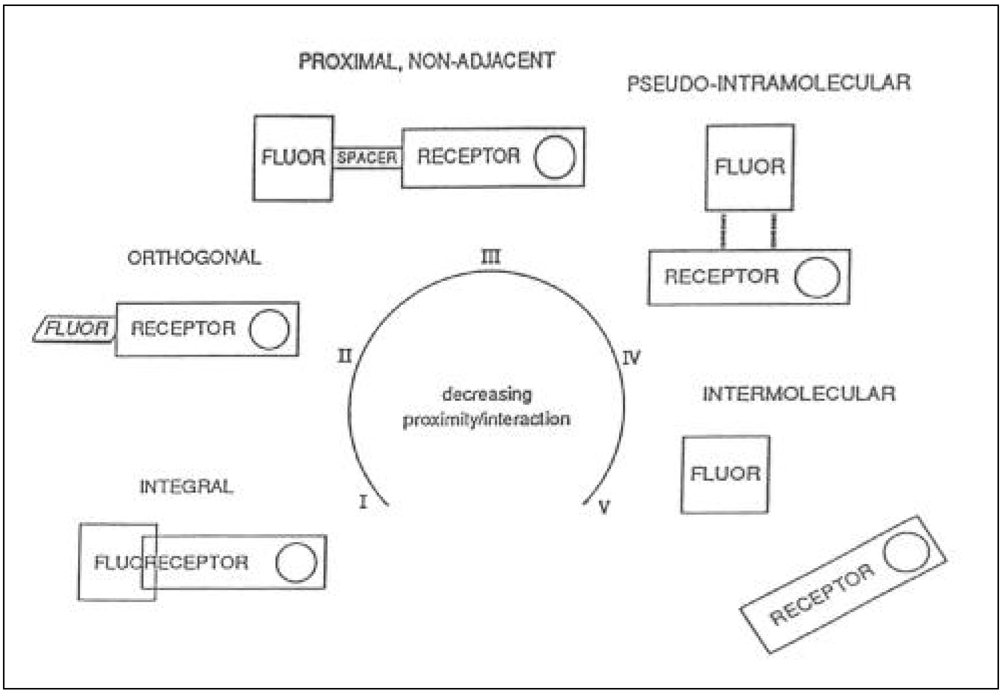

Fig. 5. Molecular structure schemes of the type 'fluor-receptor' used in fluorescent chemosensors [29].

Glass is traditionally the favourite support for optical sensors [49−51]. The special characteristics of glass, which include transparency, chemical inertness and inexpensive manufacturing procedures combine with ability to the geometric configurations and the physical characteristics of glass, make it a most suitable support for diagnostic photometry. However, due to simpler immobilisation procedures, most sensor devices utilise polymeric supports for chemical recognition phases despite their inferior optical characteristics [52, 53].

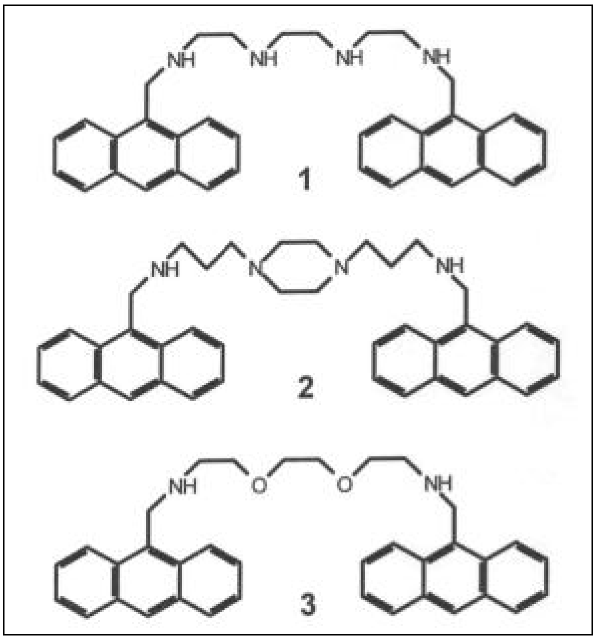

Fig. 6. Molecular structures of the studied bis-9-anthryl derivatives of the type Ant-R-Ant, where R is a quadridentate receptor spacer [63].

About ten years ago, a novel immobilising method was introduced using the sol-gel polymerisation process [5, 54, 55]. Here, the dopants are incorporated in the dry gel (xerogel) at the early stages (or even before initiation) of the hydrolysis and polycondensation processes. Thus, when the xerogel is formed the dopants remain physically encapsulated within the microporous gel matrix but maintain their ability to interact with diffusing species [56–58]. Such materials have been used in a range of recognition phase configurations. These includes monoliths and deposited films, end-coated and side-coated optical fibres and planar waveguides, and some novel configurations such as packed capillary tubes [59]. Some years ago Wolfbeis, Reisfeld and Oehme [60] have reviewed the principles of optical sensors based on the use of the sol-gel technique, in particular their fabrication, working principles, and various configurations.

In our paper [61–64] are discussed experiments with chemical recognition phases consist of the prepared fluorosensors (*bis-9*-anthryl quadridentate derivatives, Fig. 6) immobilised in porous silica xerogel by the sol-gel procedure.

The results show that the supramolecular system **1** of the type *Ant*–N–O–O–N–*Ant*, where N and O are donor atoms in the receptor (spacer or ligating) group, is the most useful as fluorosensor. This chemosensor is more sensitive for Cu(II) than for other transition metal ions such as *e.g.* Co(II), Ni(II) and Zn(II) ions (Fig. 7).

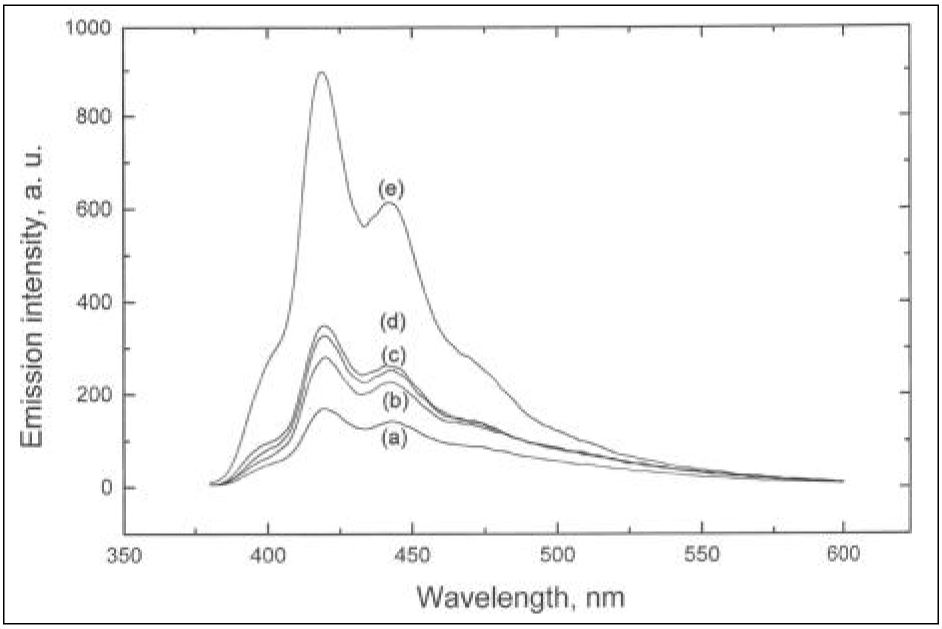

Fig. 7. Fluorescence emission spectra of the NOON fluorosensor: (a) uncomplexed and complexed with: (b) Co(II), (c) Ni(II), (d) Zn(II), and (e) Cu(II) ions [63].

Our experiments show that the sol-gel process is a versatile fabrication method to prepare chemical recognition phases of fluorescent chemical sensor. The recognition phases consist of silica as a matrix and *bis-9*-anthryl derivatives as fluorescent chemosensors for transition metal ions in aqueous solution.

Among the fluorosensors the molecular system **1**, *i.e. Ant*–N–O–O–N–*Ant,* (see Fig.) is the most promising as a component of the recognition phase in the fluorescent chemical sensor for Cu(II) ions.

4. Heterogeneous catalysts

The use of ligands stabilized transition metal clusters on the one hand and of unprotected, bare nanoparticles on the other hand as homogeneous and heterogeneous catalysts, respectively, is extensively described in the literature [65]. In particular, supported metal particles are traditionally applied in industrial catalysis for many purposes. The catalytic behaviour of bare particles on supports has been studied as a function of size and shape in a huge number of papers in the course of the last decades, whereas ligand protected clusters are much less investigated as immobilized catalysts. The main interest was focused on the function of the ligands. Indeed, they can increase or reduce activity, however, it has also been shown that the influence of ligands with respect to selectivity may also be of some interest. Schmid et al. [66, 67] have been able to show that ligand stabilized Pd clusters in the size range of 3–4 nm show very good activity and selectivity on various supports when they are used for the semihydrogenation of hex-*2*-yne to *cis*-hex-*2*-ene. The ligands consisted of variously substituted phenantrolines. It could be observed that, depending on the kind of substituent, *e.g.* alkyl groups of various lengths, the activities changed considerably, whereas the selectivity was in any case close to 100%.

On the other hand, in the case of very small Pd nanoparticles (1.5 nm) in a supported form with and without ligands to semihydrogenate hex-*2*-yne, is observed that for the phenantroline protected clusters the selectivity is only ca. 80–90%, whereas for the bare clusters it is 100 %. From experience of Schmid et al. [68] this result could not be expected. Whatever the reason for that behaviour may be, it becomes clear that catalytic studies with clusters of definite size and environment are valuable materials to work out principles.

An important progress consists of the preparation of water soluble nanoclusters using hydrophilic P- and N-donors as stabilizers [69–71]. Further miscellaneous agents have been used for this purpose [69, 72–83]. Colloidal metal systems stabilized either by surfactants or by solvents are very monodisperse and have been applied successfully as precursors to heterogeneous catalysts [84–87]. Electron microscopy has confirmed that the discrete metal particles may be deposited onto supports without and unwanted agglomeration. This is a major prerequisite for size selective studies in heterogeneous catalysis.

In our experiments we used with success amino- and thiol-trialkoxysilane derivatives as stabilizers of metal nanoparticles, such as Pd, Pt i Rh, in sol. In the next stage owing to the sol-gel process are prepared very monodisperse metal clusters supported on the organically modified xerogels. These pre-prepared nanometals stabilized by ligand amino or thiol groups may be used as easily accessible precursors for a new type of heterogeneous catalysts. These precursors may be optimized independent of the support by varying the particle size, composition, and structure of metallic system. Further, the coverage of the metal surface by various protective shells and intermediate layers, for example, oxygen or sulfur, may be used for modifications of the active component. This is visualized in Fig. 8.

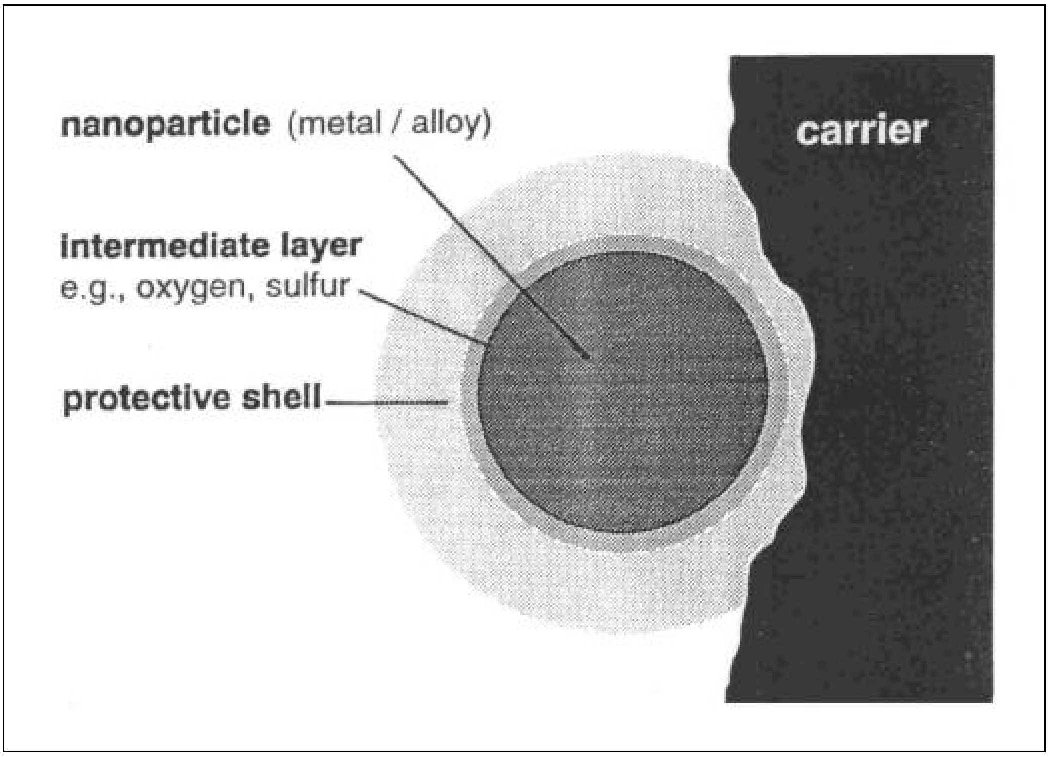

Fig. 8. The catalyst precursor concept [88].

The perfect protection of the nanometallic hydrosols by various alkoxide-derivatives allows the handling of the precursors even in concentrated alcoholic solution. Further, the use of amino- or thiol modified alkoxides as the protective shell around the metal core enables the efficient fixation the metal particles by covalent bonds on an oxide support. The supported metal particles are very resistant to agglomeration even under extreme conditions [88].

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