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Azacrown-CH_2-bipyridine receptors in silica xerogel. Optical and coordination properties†

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Samples of silica xerogel doped with encapsulated series of three receptors of the type (aza-3*n*-crown-*n*)-CH_2-(2,2′-bipyridine), where $n=4$, 5 and 6, were prepared by the sol–gel process. Fluorescence excitation spectra of the encapsulated receptors differ from the absorption spectra. Emission of the samples can be quenched specifically owing to the coordination reaction with transition metal ions. Emission decays can be described by a double exponential, the lifetime values being short at room temperature. EPR spectra of Cu^{II} ions complexed on the surface of the receptor doped xerogel have fairly well resolved hyperfine structure and show an elongated rhombic octahedral environment for the receptors with 2,2′-bipyridine groups.

Owing to the utilizing of a low temperature preparation of oxide materials, the so-called sol–gel process,[1] the previous problem related to the inability to incorporate organic molecules into an inorganic oxide glass is resolved. Using this technique, a three-dimensional network of metal-oxide bonds is formed at room temperature by the polymerisation–condensation reaction of metal alkoxides, followed by low temperature dehydration. The porous xerogel matrix thus obtained can trap receptor molecules.[2]

Inorganic oxides are superior to organic polymer matrices due to the fact that the excited state of the trapped organic molecule is capable of undergoing photochemical reactions with the surrounding organic matrix. This results in low photostability of both dopants and carrier.[3]

Silica xerogels can play the role of host matrices doped with encapsulated sensing organic indicators. The gels have the obvious advantage of chemical inertness, mechanical stability and optical transparency. What is more important, they are physically able to encapsulate the indicator molecules in pores in the gels, so that these molecules cannot be leached out in solution. At the same time the host material is sufficiently porous to enable transport of metal ions, solvent and other small molecules into the interior.[4]

Several recent observations revealed the feasibility of making optical recognition phases with receptor molecules based on silica gel for chemical sensors.[5] The exciting outcome of these observations is the feasibility of preparing gels boasting optical properties which change in the presence of target molecules. In particular, gels with receptors producing characteristic colour changes when exposed to the metal ions were prepared. It is also noted that many other organic molecules incorporated into the sol–gel optical materials exhibit luminescence throughout the UV–VIS region.[2,6] In this case metal ions penetrating a porous gel matrix can be complexed by the organic molecules which results in quenching of the fluorescence.

We are interested in investigating the spectroscopic properties and studying the behaviour of an optical material with supramolecular dopants which exhibits chemical sensing. The optical material is a silica xerogel prepared by the sol–gel method and the supramolecular dopants (Fig. 1) are receptors containing two coordinatively active subunits: 2,2′-bipyridine (with two amine nitrogen atoms as donors) and aza-3*n*-crown-*n*, *i.e.* 3*n*-membered macrocycle (with $n-1$ ethereal oxygen atoms and an amine nitrogen atom as donors). The fluorescent sensing is studied with respect to Cu^{2+} as a model transition metal ion and other transition metal ions for comparison.

The aim of this study is to prepare material which could possibly be proposed as an optical recognition phase for a chemical optical sensor. The structure of metal complexes formed after reaction with the studied receptors in silica xerogel matrix is also reported.

Experimental

Chemicals

Tetramethoxysilane, copper(II) perchlorate $Cu(ClO_4)_2\cdot 6H_2O$ (both from Fluka A.G., Switzerland), Ni^{II}, Co^{II}, Mn^{II} and Cr^{III} nitrates (from Aldrich Co.) as well as vanadyl sulfate $VOSO_4\cdot 5H_2O$ (from Merck A.G. Germany) of analytical grade were used without further purification.

The series of (aza-3*n*-crown-*n*)-CH_2-(2,2′-bipyridine) ligands (receptors) were synthesized by a preparation method similar to that in ref. 7 from azacrowns aza-3*n*-crown-*n* (abbr. A3*n*C*n*, where $n=4$, 5 and 6) and 2,2′-bipyridine (bpy), both from Aldrich Chemical Co.

Methanol and ammonia were of analytical grade purity. The water used was triply distilled from glass.

Sample preparation

The sols were prepared by a typical sol–gel procedure[1] from a starting mixture of: tetramethoxysilane (TMOS), methyl alcohol as diluent, distilled water ($TMOS:H_2O=1:4$), $NH_3(aq)$ catalyst and receptor A3*n*C*n*-CH_2-bpy. The mixture was vigorously mixed at room temperature. The sol was allowed to gel for 3 days and then dried. The xerogel obtained

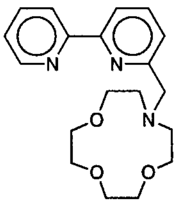

Fig. 1 Molecular structure of A3*n*C*n*-CH_2-bpy receptor, where $n=4$

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was heated for 3 h at 120 °C to remove ammonia and methanol as well as some of the water from the pores. Concentration of the receptor in the xerogel was 2.5×10^{-5} mol g^{-1} SiO$_2$. The dry xerogel was then ground in a mortar and passed through standard sieves. Particles 0.75–1.50 mm in size were immersed in aqueous solutions containing such metal ions as: Cu^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}, Cr^{3+} or VO^{2+} 200 mg (±0.1 mg) of the doped material was agitated in 0.01 M aqueous solution of the appropiate metal salt, maintaining the molar ratio [metal ion] : [receptor] = 10 : 1. The immersed xerogel was filtered off after 24 h, rinsed with distilled water and then dried. By this chemisorption method complexes with transition metal ions were formed.

The rate of uptake of the metal ions on the surface of the receptor doped xerogel was measured by cyclic voltammetry on a hanging mercury drop electrode, shaking 200 mg of the material with the metal ion solution.

Complexes of Cu^{II} with A3*n*C*n*-CH$_2$-bpy ligands (in a molar ratio 1 : 1) were also produced in the sol just before gelation. After 3 days the complexes were encapsulated by the sol–gel process in wet silica gel which was then dried.

The procedure in the case of the Cu^{II} complex with bpy differed. This complex, which was used for comparison, was formed (in molar ratio Cu : bpy = 1 : 2) separately and was dissolved in the sol before gelation. The silica xerogel with the trapped complex was obtained after gelation and drying.

Apparatus

Optical absorption measurements in the UV–VIS region were recorded on a Beckman DU 650 spectrophotometer. Spectra of the crushed xerogel samples were obtained in a silicon oil mull and were collected between 250 and 900 nm. Fluorescence emission ($\lambda_{exc} = 315$ nm) and excitation spectra ($\lambda_{em} = 360$ nm) were measured with a Perkin-Elmer LS 50B spectrofluorometer with reflection spectra attachment. None of the excitation spectra were corrected for the lamp and photomultiplier response. Fluorescence decays were measured using an Edinburgh Analytical Instruments CD 900 fluorometer.

EPR spectra were obtained on a SE/X spectrometer (Radiopan, Poznan). Sample holders were sealed quartz capillaries (1 mm diameter). A magnetic field modulation of 100 kHz was applied. Standard deviations of the EPR spectra parameters were estimated as follows: $g_{\parallel} \pm 0.003$, $g_{\perp} \pm 0.005$ and $A_{\perp} \pm 4 \times 10^{-4}$ cm^{-1}.

Results

Silica gels prepared under basic conditions (pH > 7) and high water to silane ratios produce highly branched clusters which behave as discrete species. Gelation occurs by linking clusters together.[1] This procedure makes the xerogels porous, these consequently being able to encapsulate and attach large supramolecular receptors of the type shown in Fig. 1. Probably owing to the hydrogen bond between oxygen atoms in the ether crown group and the silanol group, the receptors are practically non-leachable in aqueous solution.

Absorption spectroscopy

The receptors in methanol solution show strong absorption spectra with the characteristic band for free bpy at 290 nm (Fig. 2), whereas Fig. 3 shows room temperature absorption spectra of the receptors (and bpy for comparison) encapsulated in the xerogel. The bands for the receptors with $n = 4$, 5 and 6 are centered at 301, 299 and 298 nm, respectively. The band for the first receptor shows the greatest intensity of UV absorption among the bands compared. Compared with the bpy derivatives, the absorption spectrum of bpy is much broader but has almost the same position of the main band. Moreover, in this case, the higher wavelength wing shows comparatively higher intensity.

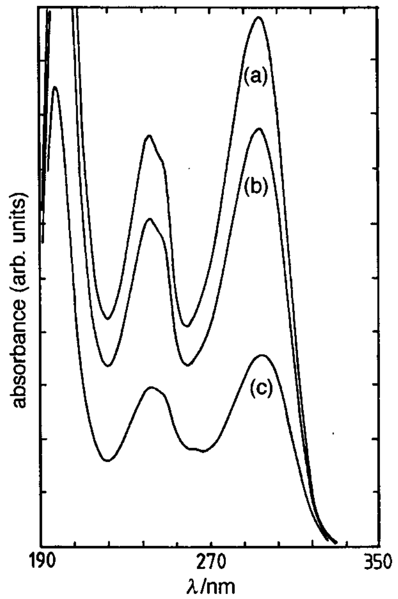

Fig. 2 Optical absorption spectra of A3*n*C*n*-CH$_2$-bpy receptors in methanol solution: (a) $n = 4$; (b) $n = 5$; (c) $n = 6$

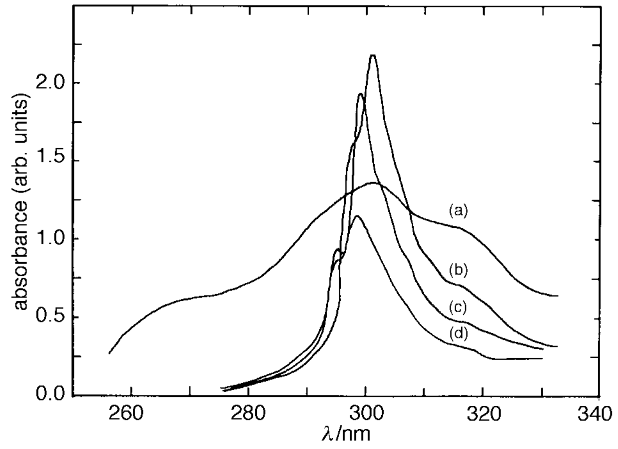

Fig. 3 Optical absorption spectra of (a) bpy, and of A3*n*C*n*-CH$_2$-bpy receptors in silica xerogel: (b) $n = 4$; (c) $n = 5$; (d) $n = 6$

Coordination process

The rate of the coordination process (see Fig. 4) indicates that complex formation on the xerogel surface is rather high

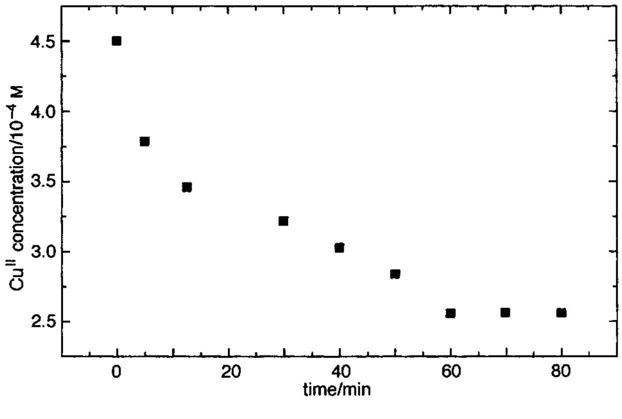

Fig. 4 Copper(II) uptake as a function of time for an A12C4-CH$_2$-bpy receptor encapsulated in silica xerogel

(measured in seconds). However, later, due to the metal enrichment within pores controlled by diffusion, a slow complexation rate is observed. In any case the maximum duration time of the process is about 60 min.

Luminescence spectroscopy

Very weak emission was observed from the xerogel samples with the bpy derivatives on excitation with light of 290 nm (absorption λ_{max}). The fluorescence excitation ($\lambda_{em}=360$ nm) and emission ($\lambda_{exc}=315$ nm) spectra of the encapsulated ligands are given in Fig. 5(A) and (B). The bands of A12C4-CH_2-bpy exhibit much higher intensity than those of the ligands with larger crown groups ($n=5$ and 6), but the band positions are the same. The excitation spectra of the bpy derivatives encapsulated in the xerogel differ from the absorption spectra [the excitation peaks are near zero at 310 nm where the species reach the maximum absorption, *cf.* Fig. 3 and 5(A)]. The emission originates from the higher wavelength wing of the absorption spectrum.

A reasonable fit of the decay curves can be achieved using the fitting functions with more than one exponential component. The best results are achieved for two exponential functions. The adequacy of this exponential decay fitting was judged by an inspection of the plots of the standard deviation and by the statistical parameters χ^2 (Table 1). In general, the two components have very short lifetimes τ. Participation of the longer lifetime is smaller and decreases with increasing *n*.

The sequence of the fluorescence quenching of the receptor with $n=6$ complexed with transition metal ions such as Cu^{II}, Ni^{II}, Co^{II}, Mn^{II}, Cr^{III} and VO^{II} is shown in Fig. 6. This sequence is similar for the complexed species with $n=4$ and 5 and is characteristic of the transition metal ions used.

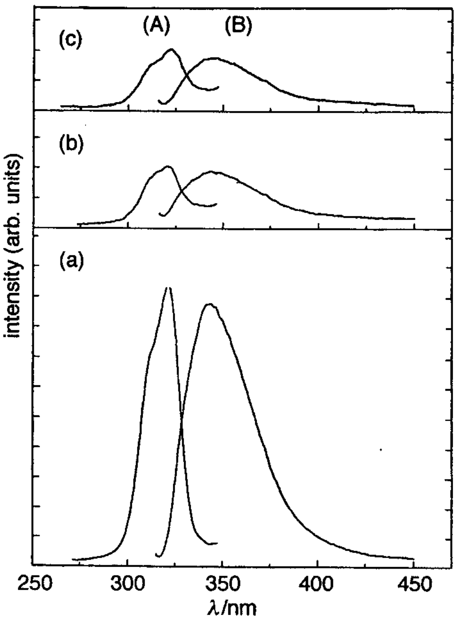

Fig. 5 Excitation (A) and emission (B) spectra of A3*n*C*n*-CH_2-bpy in silica xerogel: (a) $n=4$; (b) $n=5$; (c) $n=6$. The excitation spectra were obtained by monitoring at 360 nm and the excitation wavelength for the emission was 315 nm. Recorded at 295 K.

Table 1 Photophysical properties of A3*n*C*n*-CH_2-bpy receptors encapsulated in silica gel (measured at 295 K)

receptor, *n*	χ^2	τ/ns	contribution (%)
4	1.41	0.49	76.9
		2.1	23.1
5	1.08	0.11	99.2
		1.9	0.8
6	1.40	0.097	99.9
		2.6	0.1

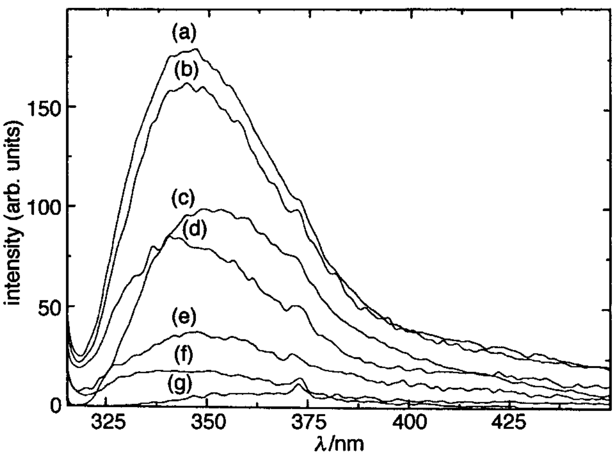

Fig. 6 Characteristic quenching sequence for A18C6-CH_2-bpy in silica xerogel, if the receptor is (a) uncomplexed; and complexed with (b) Cr^{3+}; (c) VO^{2+}; (d) Mn^{2+}; (e) Co^{2+}; (f) Ni^{2+} and (g) Cu^{2+}

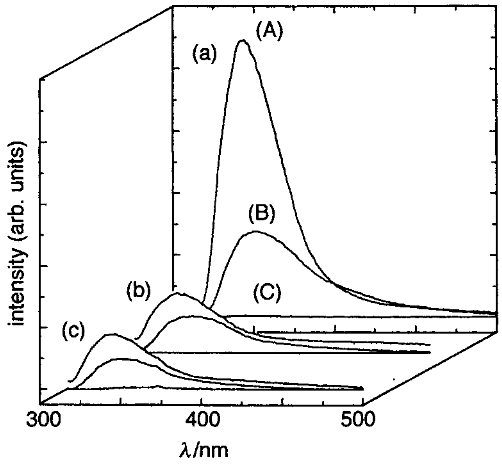

Fig. 7 Fluorescence quenching effect due to the coordination of transition metal ions in a silica xerogel doped with A3*n*C*n*-CH_2-bpy: (a) $n=4$; (b) $n=5$; (c) $n=6$. Receptors uncomplexed (A), and complexed with (B) VO^{2+} and (C) Cu^{2+}.

The room temperature fluorescence spectra of the free A3*n*C*n*-CH_2-bpy ligands in silica and complexed ones owing to coordination of the representative Cu^{2+} and VO^{2+} ions are shown in Fig. 7. Quenching of fluorescence for the complexed receptors is observed. The quenching effect is especially great in the case of the copper(II) complex with the A12C4-CH_2-bpy ligand as compared with the fluorescence intensity of the respective free receptor immobilized in silica [*cf.* in Fig. 7(a)]. The receptors complexed with Cu^{II} cation in each case exhibit near zero emission intensity, whereas vanadyl cation in this situation possesses an intermediate position among the transition ions studied.

EPR spectroscopy

EPR spectroscopy is a powerful tool with which to identify changes in the coordination environment of Cu^{II} complexed with the supramolecular entities. EPR spectra of Cu^{II} complexed with the receptors and then encapsulated in silica xerogel are shown in Fig. 8. The Cu^{II} species give rise to typical axial spectra. However, in the case of the complexes with bpy and bpy derivatives with $n=5$ and 6, the spectra exhibit two components. The hyperfine structure of the intense perpendicular signal on the high-field side is not resolved.

The EPR spectra of the samples with complexes formed by

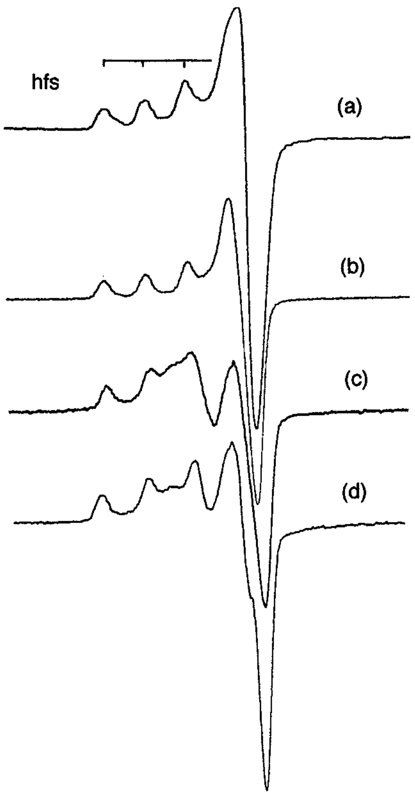

Fig. 8 X-Band EPR spectra of silica xerogel doped with: (A) Cu^{II} complexed in the reaction mixture before gelation by (a) bpy; and by A3*n*C*n*-CH_2-bpy ligands with (b) $n=4$; (c) $n=5$; (d) $n=6$. Recorded at 295 K

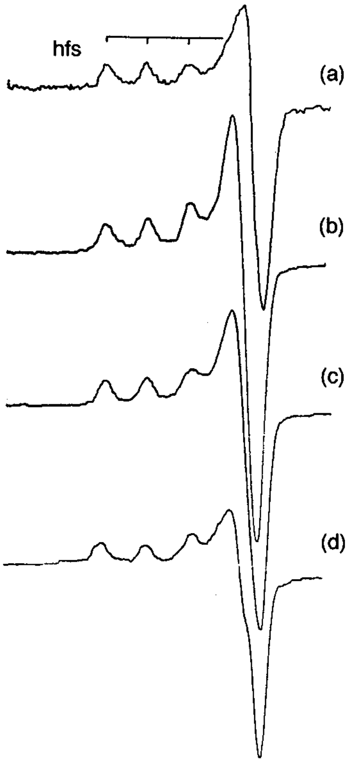

Fig. 9 X-Band EPR spectra of silica xerogel doped with (a) bpy, and with A3*n*C*n*-CH_2-bpy: (b) $n=4$; (c) $n=5$; (d) $n=6$, complexed with Cu^{II} in aqueous solution. Recorded at 295 K.

Table 2 EPR spectral parameters of Cu^{II} complexes with bpy and A3*n*C*n*-CH_2-bpy trapped in silica xerogel but formed before gelation (spectra recorded at 295 K)

ligand, *n*	$g_{\|\|}{}^a$	$A_{\|\|}{}^b/10^{-4}\,cm^{-1}$	$g_{\perp}{}^c$
bpy	2.289	154	2.055
4	2.265	154	2.041
5	2.259	158	2.033
6	2.258	156	2.027

$^a\pm0.003$. $^b\pm4\times10^{-4}\,cm^{-1}$. $^c\pm0.005$.

Table 3 EPR spectral parameters of Cu^{II} complexes formed with bpy and A3*n*C*n*-CH_2-bpy ligands in silica gel by coordination from aqueous solution (spectra recorded at 295 K)

ligand, *n*	$g_{\|\|}{}^a$	$A_{\|\|}{}^b/10^{-4}\,cm^{-1}$	$g_{\perp}{}^c$
bpy	2.280	154	2.044
4	2.257	155	2.035
5	2.258	157	2.031
6	2.258	156	2.027

$^a\pm0.003$. $^b\pm4\times10^{-4}\,cm^{-1}$. $^c\pm0.005$.

Cu^{II} ions on the surface and in the pores of the silica xerogel [see Fig. 8(b)] are similar to each other. Only in the spectrum of the sample with the $n=6$ receptor are two components clearly visible.

In view of the fact that the Cu^{II} ion concentration in the gel samples is low (about 10^{-5} mol g^{-1} SiO_2) we can neglect the possibility of interactions between copper(II) ions in the matrix. The lineshape of the EPR spectrum conforms satisfactorily with the theoretical one which is obtained assuming the spin Hamiltonian,[8] provided that the current lineshape theory developed by Kneubuehl[9] is corrected in respect of peak width.

Sets of the $g_{\|\|}$, $A_{\|\|}$ and $g_{\perp}$ values for the encapsulated Cu^{2+} complexes and owing to coordination of Cu^{II} ions are presented in Tables 2 and 3. Owing to poor resolution of the spectra, it is impossible to determine the spectral parameters for the second component in the cases mentioned above. $g_{\|\|}$ and $g_{\perp}$ differ distinctly in the Cu^{II} complexes with bpy and with the bpy derivatives on the other side, regardless of the preparation method. For all the Cu^{II} complexes, a $g_{\|\|}>g_{\perp}>g_e=2.0023$ parameter sequence is observed.

Discussion

2,2′-Bipyridine (bpy) and its derivatives are renowned for their ability to form coordination compounds with metal ions. The description, based on MO theory, of the coordinative bonds in these complexes requires that the central ion and the ligands be able to form σ- and π-bonds. It is no wonder, therefore, that bpy is a molecular block *par excellence* for a wide variety of types of supramolecular devices.[10]

Bpy, similarly to many of the optical active organic molecules tested, tends to dimerize and aggregate at moderate concentrations in aqueous solution.[11] This tendency reduces the fluorescence quantum yield significantly.[12] It is important to notice that dimerisation is greatly reduced by the trapping process in the silica xerogel, even though concentrations could be quite high (up to 10^{-2} M). The de-aggregation is a general phenomenon which indicates the lower polarity of the oxide cage[11] than water and confirms the matrix isolation of the trapped molecules.[13]

The effect is that maxima of absorption of organic, optically active molecules, are slightly red-shifted (*ca.* 5 nm) in silica xerogels, as compared with their aqueous solutions. These red-shifts confirm the slightly less polar nature of the silica cage which is composed of Si—OH (silanol) and Si—O—Si groups.[13]

It is known from previous studies[14] that bpy in alcohol at a concentration of 10^{-5} M does not aggregate, but the aggregates exist at higher concentration (10^{-3}–10^{-1} M) in water. In the latter case λ_{max} of emission is at 430 nm.[15] Thus, in the present studies (ligand concentration 10^{-5} mol g^{-1} SiO_2 and λ_{max} of emission at 345 nm) aggregation of the bpy derivatives cannot be expected. It seems that the emission is probably from the azacrown derivatives of bpy bonded to the silica network by hydrogen bonds between the silanol groups and oxygen atoms in the crown group.

The considerable intensity of fluorescence emission for silica xerogel doped with A12C4-CH_2-bpy [Fig. 5(a)] is one of the promising features for the recognition phase based on this receptor. It seems that the phase studied is suitable for selective analysis of Cu^{II} ions in solutions owing to substantial quenching of the emission by these ions [Fig. 7(a)].

The order of the emission intensity $Mn^{II} > Co^{II} > Ni^{II} > Cu^{II}$ is the reverse of the Irving–Williams order, *i.e.* order of the stabilities of corresponding complexes of the bivalent ions of the first transition series, irrespective of the particular ligand involved.[16]

The bi-exponential decay observed means that two species take part in the excitation process. Probably one of the species is the receptor supramolecule anchored with the xerogel network by hydrogen bonding and the second species is the non-bonded supramolecule. If the content of the non-bonded species decreases with n then one of the decay components decreases (*cf.* in Table 1).

The Cu^{II} ion can give numerous bis-bipyridine complexes with the general formula $Cu(bpy)_2X_2 \cdot nH_2O$. Complexes with anions which are generally reluctant to bond to the metal such as $X = ClO_4^-$ are of some interest. For these complexes the axial Cu—O bonds are considerably longer than the equatorial Cu—N bonds. It is therefore uncertain whether, in the strict sense, the oxygen atoms are bonded to the copper ion or not. Hathaway *et al.*[17–19] concluded that the compound should be formulated as $[Cu(bpy)_2](ClO_4)_2$ and that the complex cation has an essentially planar structure, although the two bpy ligands are twisted mutually by 10–30° towards a tetrahedral coordination. This is not entirely in agreement with results obtained by Nakai[20] regarding the aspect of the coordination of the ClO_4^- ion. This author presented the conclusion that in the $[Cu(bpy)_2](ClO_4)_2$ crystal the oxygen atoms complete a distorted octahedron in the axial direction, though one of the Cu—O distances is considerably longer than the other. Thus, the complex could be regarded as six-coordinate.

Since the EPR spectral parameters obey the order $g_{\parallel} > g_{\perp} > g_e$ for all of the studied coordination species (see Tables 2 and 3), it could be proposed that there exists a tetragonal coordination environment in the samples with Cu^{II} complexes prepared by encapsulation and chemisorption. Assuming that complexes of the type $[Cu(bpy)_2]^{2+}$ are unable to adopt a square-planar configuration because of steric interaction between hydrogen atoms to the nitrogen,[21] the coordination environment of Cu^{II} should be elongated rhombic octahedral.[22]

An increase of $g_{\parallel}$ indicates decreasing tetragonality of the coordination sphere of Cu^{II}.[23] It suggests that the tetragonal distortion of the complexes increases as the ligands change from bpy to bpy derivatives. In addition, this effect is greater for complexes created by the chemisorption method than in the reaction mixture before gelation.

Conclusions

The sol–gel process appears in this study to be a straightforward and versatile fabrication method for the preparation of recognition phases for optical chemical sensors.

With the help of intensity quenching experiments we investigated three different luminescent A3nCn-CH_2-bpy receptors (where $n = 4$, 5 and 6) encapsulated in porous silica xerogel. Among the samples the system with A12C4-CH_2-bpy is the most promising as a component of the recognition phase in the optical chemical sensor for Cu^{2+} ions.

The elongated rhombic octahedral environment of Cu^{II} ion complexed with ligands of the A3nCn-CH_2-bpy type (where $n = 4$, 5 and 6) consists of two bpy ligand groups in the equatorial plane.

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