Spectroscopic behavior of hybrid materials obtained by the sol–gel technique

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Abstract

The need for new, chemically and physically stable luminescent materials operating with UV excitations has stimulated research on luminescence properties of doped sol–gel material. In this work we present technology of production of silica gels doped with organic molecules, lanthanide compounds and organic/inorganic composites. Optical properties of these materials as functions of temperature, concentration and excitation wavelength are presented. Dynamics of the excited states is discussed based on the decay times and emission efficiencies data. Mechanisms of ligand-to-metal energy transfer as well as other processes affecting emission efficiency are considered. Silica sol–gels doped with di-aminoacid derivatives of porphyrins: PP(Ser)2(Arg)2, PP(Ala)2(Arg)2, PP(Met)2(Arg)2, where Met, Arg and Ser denote methionine, serine and arginine aminoacids, respectively, and H2TTMePP (tetrakis[4-(trimethylammonio)phenyl]-21H,23H-porphine) have been obtained and spectroscopically studied. The samples emit only from the lowest excited singlet state (S1). Intensity of this emission depends on the concentration of the active molecule and time of the exposition to the excitation beam. The sample containing PP(Ser)2 (Arg)2 co-doped with Tb(III) ions exhibits only 5D4 emission from the metal center. When co-doped with Pr(III) ions it displays only the S1 emission and it has been shown that the metal ions affect the S1 → S0 internal conversion. These materials can find applications as phosphors or sensors of UV irradiation. The efforts have been undertaken also to obtain chiral anisotropic materials.

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1. Introduction

Porphyrrins attract significant attention because of their role in the human body, ability to accumulate in many kinds of cancer cells as well as interesting magnetic and optical properties. These features make them useful in cancer treatment and the photodynamic therapy [1–3]. When coordinated to lanthanide ions porphyrins can be studied by electron spectroscopy of the metal centers, as well as serve as sensitizers of the ions emission. The design of efficient lanthanide complexes containing ligands having highly absorbing chromophores involves studies on cryptands [4–6], podands [4,7,8,18], macrocyclic ligands [7,9], β-diketones [10–14] etc. Enhancement of the lanthanide ions emission is of special interest because it can lead to a variety of potential applications such as electronic devices [14,15], displays [16], luminescence sensors [17] and many others.

There is also a great need for materials, which can serve as host matrices for lanthanide organic complexes, which would improve the complexes physical and chemical properties. High quality optical components possessing extremely good thermal and chemical stabilities can be produced using the sol–gel technique [13]. In this work we present syntheses and spectroscopic investigations of porphyrines derivatives and hybrid organic–inorganic materials obtained by the sol–gel route.

2. Experimental

Di-aminoacid derivatives (Fig. 1) of porphyrins: PP(Ser)2(Arg)2 (1), PP(Ala)2(Arg)2 (2), PP(Met)2(Arg)2
were obtained according to the method described in the PL patent No. 165249/B1. Ser, Ala, Arg and Met denote serine, alanine, arginine and methionine amino-acids. H2TTMePP (4) \{tetrakis[4-(trimethylammonio)phenyl]-21H,23H-porphine\} (Fig. 2) was purchased in the form of the tetra-4-tosylate salt (Aldrich) and used without any additional purification. The \[\text{Eu}(L)\text{Cl}_3\]Æ5H2O and \[\text{Tb}(L)\text{Cl}_3\]Æ4H2O complexes, where (L) denotes the podand-type ligand of the formula C36H44N8O5, were synthesized according to the method described earlier [18]. The sol–gels samples were prepared by the acid-catalysed hydrolysis of tetraethoxysilane (TEOS) with deionized water and ethanol. For comparison, some of the samples were stabilized by addition of formamide to the sols. The molar ratios [TEOS]:[formamide]:[H2O] were 11:1:6 (samples 1, 2 and 3), [TEOS]:[H2O]:[ethanol] were 1:4:8 and [TEOS]:[formamide]:[H2O] were 2:1:11 (sample 4). The sol pH was adjusted to approximately 6.5 by addition of NH3} ðaq} . Porphyrins or metal complexes were introduced to the sol in the form of aqueous solutions. In the case of the porphyrin lanthanide complexes the metal:ligand molar ratio was 4. After homogenization, these sols were allowed to gel at room temperature and were then aged for 3 months. The transparent, monolithic, free of cracks solid samples of cubic shape were obtained. We synthesized gels co-doped with two different chiral systems: podants (what was earlier confirmed by circularly polarized luminescence [19]) and porphyrins modified by L-forms of the aminoacids. Studies of the chiral behavior of the obtained gels will be described in the forthcoming paper.

Excitation and emission spectra were obtained at 293 and 77 K using a SLM Aminco SPF500 spectrophotometer equipped with a 300 W xenon arc lamp. Fluorescence lifetimes were measured using an oscilloscope Tektronix TDS 3052B and a Spectra Pro 750 monochromator. A Nd:YAG pulsed Lambda Physics laser was used as an excitation source. Absorption spectra were measured on a Cary-Varian 500 spectrophotometer.

3. Results and discussion

Let us first analyze the optical behavior of the free porphyrins doped into the silica sol–gels. All the investigated samples exhibit red emission when excited in the Soret band (around 400 nm) (see Fig. 3). This emissions correspond to the S1 → S0 transitions of the porphyrins. No emissions have been detected from the S2 excited states. This implies that the S2 → S1 internal conversion is much faster than the radiative process, the S1 → S0 internal conversion, as well as the S1 → T1 intersystem crossing. It is interesting to note the different distribution of the intensities of the respective components in the emission spectra as well as the fact that the total efficiency of the emission depends on the type of the aminoacid.

Fig. 4 shows excitation spectra of the investigated samples. The spectra consist of several bands from which the one centered at 400 nm can be ascribed as the S0 → S1 absorption transition (the Soret band) and the three bands with the maxima between 500 and 600 nm are related to the S0 → S1 absorption transition (the Q bands). In general the Soret band dominates in the excitation spectra of the investigated samples and for this reason the excitations of the porphyrins have been performed via this band (maintaining the same experimental conditions in order to compare the efficiencies of the emissions). We have also applied the selective exci-
This points to the role of the Soret band in feeding the emitting Q level. This emission is less efficient than could be expected for aminoacids derivatives of the porphyrins. It is well known that efficiency of porphyrins emission depends on agglomeration, so the observed phenomenon could be due to differences in agglomeration.

The emission intensity for the samples (1), (2) and (4) is stable in time but it changes in the case of the sample (3). As it is shown in Fig. 5, the emission intensity of the sample (3) increases during first hour of irradiation and then decreases to the 80% of its highest level (see inset). Because the emitting $S_1$ level is fed directly from the $S_2$ excited state, the process responsible for the increasing intensity must be governed by the rate of the $S_2 \rightarrow S_1$ internal conversion. At this stage of the investigations it is difficult to conclude what accounts for the observed time-dependency of the emission, but the fact that the excitation energy seems to cumulate might be important from the applications point of view. Of course, some more subtle photochemical processes can not be excluded.

The excitation spectra of the sample (4) obtained both with addition of formamide and without it show significant differences as compared to the spectra of the other samples. The Soret band in this case is split into two components and there appears a spectral “dip” at the energy where the emission maximum should be observed. This phenomenon, called surface quenching, arises from the high concentration of the active
molecules. It is well known that for solids and concentrated solutions the excitation is effective within the tails of the absorption bands only [20,21]. This effect has been also reported by us [8] and is being investigated in more details at present.

It is worth stressing that addition of formamide affects significantly transparency of the gels, intensity of their emissions and color of the samples. Transparency of gels depends also on the homogenization level of the starting solutions. Furthermore, these processes are irradiation-dependent and reversible.

We have studied also the influence of the lanthanide ions on the emission behavior of the porphyrins-doped silica sol–gels. Two metal ions were chosen: Tb(III) and Pr(III). In Fig. 6 the absorption, excitation and emission spectra of the compound (1) coordinated to the Tb(III) ion are presented. The conclusions stemming from the analysis of the presented spectra are rather confusing. As can be seen, the sample displays only green metal-centered emission associated with the transitions from the 5D4 excited state of the Tb(III) ion. No emission from the porphyrin has been detected. The absorption spectrum shows presence of both the Tb(III) ions and porphyrin molecules in the sample. It consists of two well pronounced bands located at around 285 and 408 nm. The first one can be defined by the absorption transitions to the higher excited states of the Tb(III) ion (5H6, 5H5, 7F6, 5D1, 7F6, 5G3, 5L8, 5L7, 5L6, 5G2, 7F6) and the second one as the Soret band of the porphyrin. There are also some very weak bands, which can be related to the transitions from the 7F6 ground state to the 5D3, 5G6, 5L10, 5G5, 5D2, 5G4, 5L9 excited states of the Tb(III) ion. The excitation spectrum, recorder by monitoring the emission at its maximum, consist only of the Tb(III) ion absorption transitions. This is a clear evidence that the ligand-to-metal energy transfer process does not take place. If it would be so, the porphyrin should emit under excitation within the Soret band, which is not the case. The 5D3 excited state of the Tb(III) ion is located very close to...
the S₂ singlet state and ⁵D₄ emitting level of Tb(III) is located between the S₂ and S₁ singlet states of the porphyrin (see Scheme 1). This creates possibility for the ligand-to-metal and back-energy transfer processes to occur. The latter process is well known for Tb(III) ions attached to organic ligands and was reported for solids and solutions [22,23]. The back-energy transfer would lead to quenching of the Tb(III) ion emission, which is also not the case. Thus, the porphyrin ligand, being a component of the gel, is inactive from the emission point of view and does not participate in the energy transfer processes. Because the sol–gel samples doped with the free porphyrin do emit, the role of the Tb(III) ions in quenching its emission is apparent. At this stage of the investigations we are not able to propose a reasonable mechanism explaining this fact.

The sol–gel sample doped with the ligand (1) and the Pr(III) ions exhibits quite different optical behavior as compared to the Tb(III) sample. Fig. 7a shows emission spectrum of the Pr(III) sample under excitation within the Soret band (~400 nm). The spectrum is virtually identical to that of the free porphyrin-doped sol–gel matrix. The metal-centered luminescence has not been recorded with the independent excitations performed through the ligand and metal absorption bands. Because the ³P excited state manifold of the Pr(III) ion is located between the S₂ and S₁ singlet states of the porphyrin (see Scheme 1) a question arises whether the Pr(III) excited states mediate the S₂ → S₁ internal conversion. In Fig. 7b the excitation spectrum of the Pr(III) sample is plotted. The lack of the sharp bands of the Pr(III) ion suggests that there is no energy transfer between the Pr(III) ion states and the S₁ excited state of the porphyrin. However, the intensity ratio of the Soret/Q bands, which is much higher than for the free ligand (compare Figs. 4 and 7b), indicates that the ³P excited state manifold of the Pr(III) ion influences the internal conversion process. However, the Pr(III) ion role is still not clear.

The same Pr(III) complex has been also investigated in aqueous solutions. The S₁ emission intensity exhibits strong dependence on the Pr(III) ions concentration. It increases as the concentration of Pr(III) ions increases, reaches maximum and starts to decrease (see Fig. 8). Please, note the appearance of the additional band (as

![Scheme 1. Energy level diagram of the excited states of porphyrin, Pr(III) and Tb(III).](image1)

![Fig. 7. Emission (a) and excitation (b) spectra of the PP(Ser)₂(Arg)₂:Pr(III)-doped silica sol–gel sample.](image2)
compared to the sol–gel sample) located at around 575 nm. Apparently, the presence of the Pr(III) ions in the solution influences the S1 porphyrin emission. To our knowledge this is the first observation of this phenomenon. We expect that the role of the lanthanide ions in this process might be discovered after conducting systematic studies at different concentrations of the investigated compound in water solutions and in sol–gel matrices as well as for different excitation energies. This work is in progress.

The subject of our investigations have been also the [Eu(L)Cl3]·5H2O and [Tb(L)Cl3]·4H2O complexes incorporated into silica sol–gels. Spectroscopic characterizations of the solid complexes as well as their solutions were reported by us previously [5]. Both sol–gel samples display typical metal-centered emissions when excited within the ligand absorption band at 320 nm (see Figs. 9 and 10). The emission spectra are associated with the radiative transition from the 5D0 excited state of europium or the 5D4 excited state of terbium. The emission spectra of the sol–gel samples differ from those of the respective aqueous solutions. This can be due to the interactions between the silica matrix and the entrapped compounds or/and the deformation of the complex structure induced by the rigid host material.

When measurements are performed at low temperatures (77 K), the Eu(III) sol–gel sample emits (in addition to the metal-centered emission) blue–green light of

Fig. 8. Influence of the Pr(III) ions concentration on emission intensity of PP(Ser)2(Arg)2:Pr(III) in aqueous solutions. The inset shows extended part of the spectrum marked as (1).

Fig. 9. Emission spectra of TbL·4H2O-doped silica sol–gel matrix (a,b) and the complex aqueous solution (c).
the ligand origin (Fig. 10). The Tb(III) sol–gel sample does not exhibit the additional emission at low temperatures (Fig. 9). This suggests existence of only one mechanism of radiative relaxation for the Tb(III) sample i.e. the direct energy transfer from the ligand excited states to the metal ion excited states. In the case of the Eu(III) sample the emitting excited state (5D0) is located at lower energy compared to the Tb(III) excited state (5D4), giving rise to competition between the radiative transition from the ligand excited state and the energy transfer from this state to the europium ion excited states. This can be explained by taking into account the selection rules for the transitions mentioned above. The ligand triplet state is almost in resonance with the 5D4 emitting level of Tb(III) (ΔE ≈ 3000 cm⁻¹) what creates proper conditions for direct energy transfer between them. In the case of the Eu(III) sample the respective levels are far from resonance (ΔE ≈ 6000 cm⁻¹) and the energy transfer could occur involving the 5D1 and 5D2 excited states. Since the selection rules allow only direct energy transfers to the 5D1 level by the exchange mechanism and to the 5D2 level by the dipole-dipole and dipole–multipole mechanisms, the energy transfer to the 5D0 level is forbidden. For this reason the rate of the intersystem crossing within the ligand molecule and the rate of the energy transfer to the metal center become comparable. As a result, the spectrum consists of both ligand- and metal-centered emissions. It is well known that sol–gel silica matrix itself can emit in the visible region under laser excitations. Under the xenon arc lamp excitation (which is our case) the emission from the sol–gel matrices has been recorded only at low temperatures. It is much weaker than the emission from the Eu(III) sample and is located in the blue region of the spectrum.

Our first observation of such bright blue-green emission of the sol–gels doped with organic ligand coordinated to lanthanide ions concerned Eu(III) and Tb(III) complexes with dipicolinic acid and its more bulky derivative: 4-phenyl-ethylidipicolinic acid [24]. The detailed considerations of the mechanism of this process will be presented in the forthcoming paper.

Table 1 collects the luminescence lifetimes obtained for the investigated sol–gel samples. In our earlier work concerning the Eu(III) podant [8] we described the presence of two forms of the complex in solutions (with an exception of CH₃CN). A two-exponential fitting procedure applied for the decay curves recorded for the Eu(III) and Tb(III) podants, proved the existence of the two forms also in the rigid matrix.

The decay time for the PP(Ser)₂(Arg)₂:Tb(III)-doped sol–gel sample (1.13 ms) is much longer than in the case of the Tb(III) aqua ion (0.467 ms) [25]. This indicates that the porphyrin is coordinated to the metal ion. The decay times of the porphyrins co-doped into the silica gels are longer than those obtained for the porphyrins at the same concentrations in solutions. This shows the role of the matrix rigidity in stimulating more efficient emission.

4. Summary

1. The emission intensity of PP(Met)₂(Arg)₂ incorporated into the silica sol–gel matrix increases in time reaching saturation after approximately 1 h and than it decreases to 80% of its highest level.
2. The emission intensity of H₂TTMePP depends on the Pr(III) ions concentration in solutions. It increases as concentration the of Pr(III) ions increases, reaches maximum and starts to decrease.
3. The PP(Ser)₂(Arg)₂ doped sol–gel samples display only metal-centered luminescence when co-doped with the Tb(III) ions and ligand-centered luminescence in
the case of the Pr(III) co-doping. For the latter system the spectrum differs from that of its aqueous solution.

4. The sol-gel matrices doped with the Eu(III) and Tb(III) complexes of the podand-type ligand display the typical metal-centered emissions when excited around 320 nm. The spectra differ from those of their aqueous solutions.

5. The sol-gel sample doped with the Eu(III) podant displays blue-green luminescence at 77 K (contrary to the Tb(III) sample) in addition to the metal-centered emission.

References