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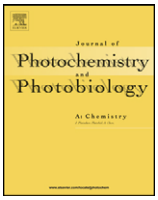

Axially substituted ytterbium(III) monophthalocyanine—Synthesis and their spectral properties in solid state, solution and in monolithic silica blocks

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ABSTRACT

The axially substituted monophthalocyanine complexes of lanthanides are not enough investigated in comparison with sandwich-type phthalocyanine complexes of lanthanides because of their much lower stability in comparison with sandwich-type complexes. In this work, the new methods of obtaining monolithic silica blocks doped with acetato substituted Yb(III) monophthalocyanine complex are reported. The spectroscopic properties of this complex were measured and the results were compared for solution, solid state and xerogels dotted with PcYb(OAc). Besides of the usually observed emission of the phthalocyanines, the emission of the Yb^{3+} ion in IR region after excitation in phthalocyanine band (674 nm) for Yb(III) complex incorporated in silica gel was observed first time. Thus, this result confirms energy transfer in the system under study. The mechanism of energy transfer was proposed. It is worth to notice, that Yb(III) emission was not observed for complex in solution and at solid state. The IR and Raman spectra of ytterbium ion in phthalocyanine complexes are reported and discussed.

1. Introduction

Phthalocyanines (Pc) are the large family of compounds, and during the past decade phthalocyanines have gained considerable attraction of scientists and technologists owing to their optical and electrical properties [1–3]. Monophthalocyanines or metallophthalocyanines (termed as MPc) consist of phthalocyanine ring coordinated to a metal, placed in the central cavity. MPc species can be synthesized from more than 70 metallic and metalloid atoms, Fig. 1a, and phthalocyanine complexes of rare earth metal constitute a very broad and important part of this family [4]. Besides this variety of phthalocyanine structures, Pc's permit chemical modification through change of the central metal ion and through axial ligation to the central metal. The phthalocyanine fragment is also capable of vast versatility through symmetric and asymmetric substitution of the main phthalocyanine skeleton or by modification of the ring system [2]. Phthalocyanine can also form double-decker ($LnPc_2$) and triple-decker rare earth complexes, Fig. 1b [5]. Most works devoted to lanthanide complexes of phthalocyanines concentrate on this group of species. This wide range of possibilities explains the vast number of phthalocyanine molecules synthesized until now and the increasing number of Pc molecules that are used and tested in different areas of science and technique. Metallophthalocyanine compounds have attracted special attention due to their unique properties such as conductivity, electrochromism and a variety of catalytic functions. Phthalocyanines are characterized by significant absorption in the visible region, large absorption coefficient, and high thermal and photochemical stability. For that reason they are good potential candidates for solar-to-electric energy conversion and as modulators of light energy in laser devices [1,6–9]. As a model system for phthalocyanine basic solar-to-electric energy converters, optical data carriers, chemical sensors and laser devices, we can use sol–gel materials doped by metalloporphyrins and their analogues – metallophthalocyanines [10–12]. It is a new mixing organic and inorganic hybrid material with unique physical, chemical and optical properties. Sol–gel monolith and sol–gel thin films are very useful to encapsulate various guests such as inorganic clusters [13–15], lanthanide complexes [16,17], laser dyes [18,19], etc. Different complexes, including metalloporphyrin and metallophthalocyanine based systems, have also been encapsulated by sol–gel processing to give materials wide spectrum of usage abilities [20–25]. Moreover, sol–gel materials have been intensively investigated as host media to encapsulate different spacious biological materials, including enzymes, catalytic antibodies, proteins, polynucleic acids, microbials, animal cells and plants for applications in biocatalysis, immunodiagnostics, bioptical devices and as biosensors or bioimplants [26].

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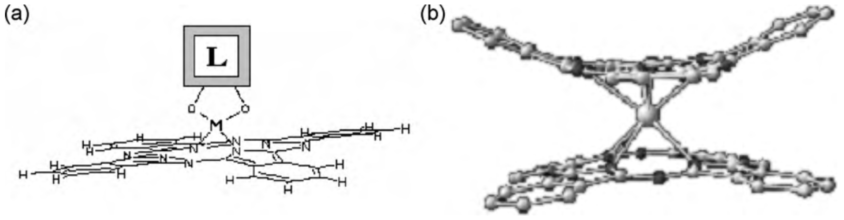

Fig. 1. Axially substituted metallophthalocyanine (a) and bisphthalocyanine of lutetium (b) (ACD optimized structure [29]).

The axially substituted monophthalocyanine complexes of lanthanides are not enough investigated in comparison with sandwich-type phthalocyanine complexes of lanthanides because of their much lower stability in comparison with sandwich-type complexes. However, there are some opinions that registration of lanthanide emission in monophthalocyanine (half-sandwich) complexes is impossible, and only last few years appeared the works, where the emission of central coordinated lanthanide ions in monophthalocyanine complexes was reported [27]. The basic aim of our work was the synthesis of soluble axially substituted phthalocyanine complex of lanthanide, incorporation of phthalocyanato-metal complexes into silica gel with the use of sol–gel method, and comparison of the spectroscopic properties of obtained complex in solution and in monolithic silica blocks. This method creates new possibilities of investigation of monophthalocyanine complexes of lanthanides. The structure of molecules of MPc becomes more stable in micropores of gel and the chemical interaction between silica matrix and central metal atom and ligands can take place, as it was described earlier [28,29]. The ytterbium complex of phthalocyanine was chosen for experiment for two reasons. First of all, this complex is soluble in polar organic solvents, used in sol–gel method (in range of aceto-lanthanide complexes of phthalocyanines which were obtained by our group, the Ce formed only the sandwich-type complex, the complexes of metals from Nd to Eu were insoluble in polar solvents, Tb and Gd complexes have low solubility and complexes of lanthanides from Dy to Lu were solved in polar solvents in a scale 5×10^{-4} M concentration). Conversely, in the range of soluble complexes (Dy–Lu) only Yb has one emission transition in NIR region which is not cowered by much more intensive red emission of π-conjugated system of phthalocyanine or overlapped by upconversion transitions, thus can be registered with available instrumentation methods.

2. Materials and methods

All commercial reagents, sol–gel precursors and solvents were used without further purification.

2.1. Synthesis of ytterbium(III) phthalocyanine

PcYbOAc was obtained by heating Na_2Pc (Merck, Germany) with $Yb(OAc)_3 \cdot 3H_2O$ (ABCR, Germany) (molar ratio 1:1.1) in DMSO (Merck, Germany) about 150 °C for 5–8 h. Then, the obtained solution is cooled to 70–80 °C, filtrated to extract insoluble residue and water is added to the solution. The mixture is left overnight in order for the precipitate to form. The formed product is filtrated and washed with large amounts of water. If it is necessary for purification, obtained complex re-precipitates from mixture DMSO–water. Yield: about 25–35%.

2.2. Synthesis of PcYbOAc dotted monolithic silica blocks by sol–gel method

Method I – TBOS (ABCR, Germany) based sol–gel method, when DMSO solution of PcYbOAc was added to reaction mixture before gelling. A solution, mixed in mole ratios, of tetrabutyl orthosilicate $(C_4H_9O)_4Si$:n-butyl alcohol:water:HCl = 350:150:10:1 was heated and stirred at a temperature of 120 °C for 3 h, whereby the solution used for a sol–gel method was synthesized. The appropriate amount of complex solution in DMSO was added and stirred.

Method II – Impregnation of TEOS (Fluka, USA) and TBOS (ABCR, Germany) based xerogels with DMSO solution of PcYbOAc. As the alternative method we use the impregnation of dried gels (xerogels) in DMSO solution of investigated complexes ($C_m = 2 \times 10^{-4}$ M).

For the spectral investigation of probes, the following instruments had been used: for registration of absorption spectra of PcYb(OAc) in UV–vis–NIR region in solution (MeOH, DMSO) and in solid state (suspension in paraffin oil) – spectrophotometers Specord M42 (Carl Zeiss, Jena) and Varian Cary 500 SCAN UV-VIS-NIR; corrected excitation and emission spectra of PcYb(OAc) were measured at room temperature and 77 K for metal complexes in DMSO and MeOH solutions ($C_m = 2 \times 10^{-5}$ M in quartz cell) and in solid state (quartz tube) using SLM Aminco SPF spectrofluorometer equipped with 300 W xenon lamp or ARC Spectra Pro 750 monochromator equipped with Hamamatsu R 928 photomultiplier as the detector. 450 W xenon arc lamp was used as the excitation source. It was coupled with 275 nm excitation monochromator which used a 1800 l/mm grating blazed at 250 nm. The excitation spectra and lifetime of fluorescence of PcYb(OAc) dotted silica gels were registered with pulsed laser Nd-YAG with Optic Parameter Oscillator (OPO), Double grating monochromator GDM-1000 (250–1400 nm, 1200 l/mm), IR photomultiplier R 406, with PbS detector Janson J10D PbS-020-TE-H (1000–2800 nm) and IGA 030-TE2-H (800–1700 nm); Fourier transform infrared spectra (FTIR) of complexes in KBr pellets in room temperature were measured in the 5000–30 cm^{-1} range using the BIORAD 575 spectrophotometer with a 2 cm^{-1} resolution. Room temperature FT-Raman spectra (FT-Raman) were measured in the 4000–80 cm^{-1} range using BRUKER 110/S spectrometer with the Nd:YAG excitation and 2 cm^{-1} resolution.

SigmaPlot 8.0 (SPSS Inc.), ACD/Spec Manager 4.60 (Advanced Chemistry Development Inc.) and OriginPro 7.5 SRO (OriginLab Corp.) programs were used for spectral data processing.

3. Results and discussion

3.1. Optical properties of PcYb(OAc) in solution and solid state

3.1.1. Absorption and emission spectra in UV–vis–NIR region

Absorption and emission spectra of lanthanide complexes of phthalocyanines were investigated and are displayed in appropriate figures (Figs. 3–7). In UV–vis spectra of PcYb(OAc) in solution we observed two bands of HOMO–LUMO transitions of π-conjugated system (N_8 moiety) of phthalocyanine macrocycle (Gouterman's four orbital LCAO model). The band of permitted a_{2u}–e_g transition $\pi \rightarrow \pi^*$ (named Soret or B band) with λ_{max} about 342 nm and forbidden a_{1u}–e_g transition $\pi \rightarrow \pi^*$ with λ_{max} about 675 nm [2,30] (Fig. 2a). The maximum of Soret band delicately shifted (1–5 nm) to longer waves with erase of concentration of the complex, but

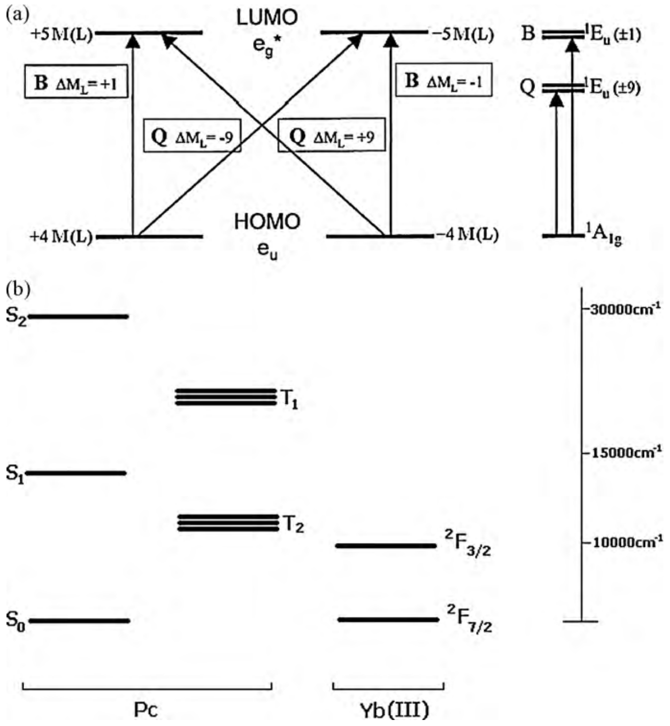

Fig. 2. Gouterman's four orbital LCAO model scheme (a) [30] and theoretical scheme of energy stages of PcYbOAc molecule (b).

Lambert–Beer linearity was kept in the range of the concentrations 10^{-6}–10^{-4} M. It means that in this concentration range, we did not observe the dimerization or further agglomeration processes, and complex is in monomer form. It is important to note that PcYb(OAc) is stable only in absolute, anhydrous solvents (MeOH, EtOH, DMSO), as it was checked by using the absorption spectra measurement. Some authors erroneously described such changes in absorption and emission spectra of lanthanide complexes as dimerization and agglomeration processes [16]. The presence of trace amounts of water in solvent caused demetalization of the complex. It is manifested in additional splitting of the Q band in the comparison of absorption spectra of PcYb(OAc) in solution and in solid state (suspension in paraffin oil). Fig. 3 shows that absorption spectra of the phthalocyanine complexes are point at the strong agglomeration in solid state. On the other hand, the transition of Yb(III) ion in the MPc should be expected in the measured spectral range. The important observation is that the absorption maxima of coordinated lanthanide ion were not registered for investigated complex in solid state and in solutions. The $^2F_{7/2} \rightarrow {}^2F_{5/2}$ Yb(III) transitions intensity in the conditions of absorption spectra measurement of the metallophthalocyanine complex in solution (10^{-4} M) and in oil is too low to be observed. Moreover, the effect of covering the ytterbium (C-T) absorption bands in UV and $^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition in NIR region by wide B band and very intensive Q band of phthalocyanine macrocycle is possible

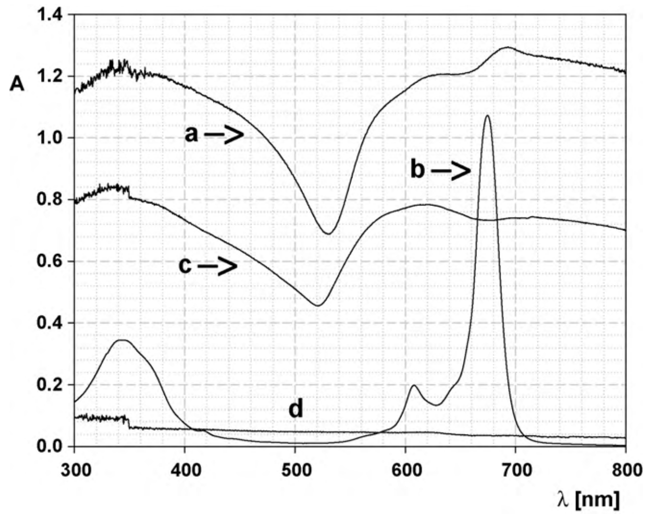

Fig. 3. Comparison of absorption spectra of PcYb(OAc) in solid state (a), in DMSO solution (C_m=1 × 10^{-5} M) (b), free phthalocyanine (H_2Pc) in solid state (c), and pure paraffin oil (d).

3.1.2. The emission spectra of PcYb(OAc)

Fig. 6 shows the relative strong emission of phthalocyanine macrocycle in DMSO and absolute MeOH solution at room temperature and at 77 K in visible region (λ_{exc} = 612 nm, maximum of satellite bond in Q region), but the emission bond of ytterbium(III) from $^2F_{5/2}$ state in near infrared region (about 980 nm) and/or charge transfer emission was not registered. It is worth noticing that the emission was excited by strong Q band, thus one can expect efficient energy transfer from phthalocyanine triplet and singlet states to $^2F_{5/2}$ Yb(III) state (Fig. 2b). Moreover, the condition of energy transfer in our system seems to be even better than for appropriate Yb(III) porphyrins, for which emission from $^2F_{5/2}$ state was reported [31–33]. In our opinion, there are few reasons of absence of emission signal from Yb(III) state in solutions. First of all, the maximum concentration, which can be obtained for PcYb(OAc) in DMSO or MeOH solution, is about 10^{-4} M. The maximum concentration is limited by solubility of complex in these solvents, and partial concentration of lanthanide in this system is too low for registration of emission, although energy is transferred from ligand states. The second reason is that emission of metal is quenched by internal vibration of solvent molecules and ligands. In the system under study the solvent molecules can complete the coordination of Yb(III) ion to 8 or 9, thus they should participate in emission quenching.

Moreover, in energy transfer process the charge transfer (C-T) Yb(III) ion state should be considered, as we have reported the results of the spectroscopic studies and calculations, and discovered that C-T state decreases quantum yields when its energy is close to ligand singlet states [13,34,35]. Since C-T Yb(III) ion state is located at rather high energy, thus close to phthalocyanine singlet states. Besides, the acetate singlet and triplet states should also be taken into account in the analysis of the energy transfer. The positions of maxima in emission spectra depended on concentration of complexes. We failed in our attempt to detect the low temperature emission of investigated complex in solid state (PcYb(OAc) powder). Neither emission bands from π-conjugated system of phthalocyanine, nor bands of electron transitions of central lanthanide atom or charge transfer were observed. Self-quenching is responsible for block of the emission from S and T states of Yb(III) phthalocyanine in solid state, and Xe lamp was too weak to excite the Yb(III) $^2F_{5/2}$ emission. The maxima of emission band of DMSO solution of PcYb(OAc) with higher concentration were wider and shifted about 40 nm to infrared region (see Fig. 6), that correspond to aggregation processes, which took place in solution and that was observed also in absorption spectra (Fig. 3).

3.1.3. IR and Raman spectroscopy

Infrared (IR), Raman (R), resonance Raman (RR), and surface enhanced resonance Raman scattering spectroscopy (SERRS) have been used to study the 1:1:1 lanthanide phthalocyaninate mixed-ligand derivatives. IR spectroscopy has often been used to check the purity of the phthalocyaninate derivatives, and especially to detect the presence of metal-free phthalocyanines, $H_2(pc')$ which

Table 1
The wave numbers of the main bands in IR and Raman spectra of PcYb(OAc), and correspondence of these bands to vibrations of bonds in molecule PcYb(OAc).

IR	RS	Assignment
3291vs, 3074vs		ν(HB)
3047s	3022vw	ν(CH)
2540s	2800vw, 2570vw	$\nu(CH_3)+\nu(CH_2)$
1617m, 1607m, 1598m, 1580w	1602vw, 1711vw	ν_{ii}
1536m, 1523m, 1502s	1543vw, 1509vw	ν_{as}(CNC)
1477s	1469w, 1446m	$\delta_{as}(CH_3+CH_2)$
1460m, 1438s, 1402m, 1383m	1435m, 1419w, 1404w, 1397w, 1389w	ν_{ii}
	1369s	$\delta_{as}(CH_3+CH_2)$
1362m, 1333s, 1320s	1347s	ν_{ii}
1304s, 1276m, 1251m, 1186m	1288m, 1266s, 1247m, 1181vs	δ(CH)
1158m		ν(CO)
1119s	1145sh	δ(CH)
1110m	1108w	ν_{ii}
1093m		δ(CH)
1068m, 1044w, 1006s, 975sh	1066w, 1062w, 1046w, 1026w, 1013w, 998w, 974w	δ_{ii}
950sh, 941w	963m, 952w, 946w, 936w, 923w	δ_{ii}
	896w, 886w	ν_s(CNC)
874m, 849w	880w, 858vw	$\delta_{ii}+\delta$(CNC)
765m	821vw, 796vw, 756vw, 749vw	δ(CNC)
735s, 730s	747vw, 726w	ω(CH)
714s, 684w, 639w	712vw, 690m, 662m, 640w	Pc breathing
639w, 617w	626w, 607vw, 591s	γ(CNC)
566s, 555w, 528vw, 499vs, 493vs, 488w, 461s, 432w, 416vw	567w, 543vw, 494w, 477vw, 466vw, 429vw, 420vw, 409vw	$\gamma_{ii}+\gamma_{Pc}$
375m, 362m, 354m, 334m, 315m, 303m, 281s, 260m	373vw, 366vw, 313vw, 274vw, 248vw, 244vw, 242vw, 235vw	ν(LnO)
246m, 227m, 209m, 202m, 194m	215vw, 195vw	$\nu(LnN_4)$
187m, 181m, 176m, 173m, 170m, 157m, 150m, 133m	178vw, 162vw, 156vw	$\delta(NLnN_4)$ δ(OLnN)
133m, 126m, 122m, 105w, 100w, 92vw, 89vw, 81vw		δ(NLnN) + (OLnO)
68vw, 62vw, 56vw		

HB, hydrogen bond; ii, isoindole.

show the characteristic band near 1008 cm^{-1}. The presence and mode of coordination of the β-diketonate and acetate anions and the molecules of salvation have also been studied by IR spectroscopy via their ν(C–O), ν(C–C) and ν(O–H) characteristic bands [36].

The basic aim of IR and Raman spectral investigations was to obtain additional information about purity and structure of obtained complex. The theoretical interpretation of PcLn(OAc) spectra, based on literature data for other phthalocyanine complexes with p-, d- and f-elements and theoretical researches, was presented in our previous work [37]. Due to this interpretation, the wave numbers of the main bands in IR and Raman spectra of PcYb(OAc), and correspondence of these bands to vibrations of bonds in molecule are presented in Table 1, and the statements which can be pronounced on the assignment of the observed bands to the respective normal modes were presented below.

First of all, in IR and Raman spectra we can see the range of evident confirmations that the obtained compound is a monophthalocyanine complex of ytterbium axially substituted with acetate. The first important observation is that the strong characteristic band, situated about 3400 cm^{-1} in IR spectra, and originated from stretching ν(NH) vibrations, described for metal-free phthalocyanine, is decayed. It proves the bond formation between the Pc ligand and Ln^{3+} ion. On the other hand, the vibrations of the OAc ligand are observed in the well defined for the CH_2 and CH_3 regions [38]. The bands at about 1140 cm^{-1} are tentatively assigned to the stretching ν(C–O) vibrations.

Also, the tree types of isoindole skeleton vibrations are observed in appropriate regions: stretching 1540–1620, 1300–1490, 1100–1120 cm^{-1}, in-plane bending 900–1010, 840–860 cm^{-1} and out-of-plane bending 320–550 cm^{-1}. The modes corresponding to the coupled vibrations of the whole Pc system appear in the regions: 620–690 and 320–500 cm^{-1}. The four types of motions corresponded to aza-bonds vibrations: in-plane stretching modes ν_{as}(CNC) at 1500–1525 cm^{-1}, ν_s(CNC) at 860–880 cm^{-1} and δ(CNC) at 740–775 cm^{-1} as well as out-of-plane bending γ(CNC) at 500–580 cm^{-1}.

The shape of several multiplets in the region 500–1700 cm^{-1} allows to identify them as doublets. For example a clear splitting is observed for PcYb(OAc) complex in the IR spectra at 1502/1523, 1276/1304, 1320/1333, 1186/1196. 1110/1119, 714/735 and 616/639 cm^{-1} as well as in the Raman spectra at 1146/1162, 1124/1127, 1037/1045, 858/879, 712/715, 494/505 and 473/477 cm^{-1}. Such behaviour suggests that the planar Pc system built from four isoindole units is deviated in the PcLn(OAc) complex. The N_8 plane is bent along the axis passing through two opposite nitrogen atoms of the aza-bonds. The symmetry of the whole unit could be approximated by the C_{2v} symmetry.

In the very broad IR contour in the range 50–300 cm^{-1}, two clear multiplets are registered. In the range 200–300 cm^{-1} four bands are contained which correspond to the four stretching ν(Yb–N) vibrations of the YbPc system, at 281, 260, 246 and 227 cm^{-1}. Also, in IR spectrum we can find the band at 176 cm^{-1} which can be assigned to the ν(Yb–O) vibration of the Yb–OAc bond. Another multiplet, which is observed in the range 50–160 cm^{-1}, consists of the components at 157, 150, 133, 122, 105, 88 and 56 cm^{-1}, and corresponds to the bending $\delta(LnN_4)$ vibrations of the first coordination sphere of the complex. The shape of the four clear components for the stretching $\nu(LnN_4)$ bands indicates that the structure of the coordination polyhedron in the PcLn(OAc) complexes is strongly distorted and the local symmetry of the Ln^{3+} ion is C_1. This type of structure is known, and often occurs in works devoted to XRD studies of metal–phthalocyanine complexes [39].

3.2. Silica gels obtained by sol–gel method and dotted by aceto ytterbium(III) phthalocyanine

3.2.1. Synthesis of PcYb(OAc) dotted transparent monolithic silica blocks and their absorption and emission properties

The standard strategy of dotting of silica gels by metallophthalocyanine complexes that was used for zirconium and hafnium complexes in our earlier works [28,29], is absolutely not suitable for lanthanide complexes of phthalocyanines. Lanthanide phthalocyanine complexes were demetalized in conditions of reaction

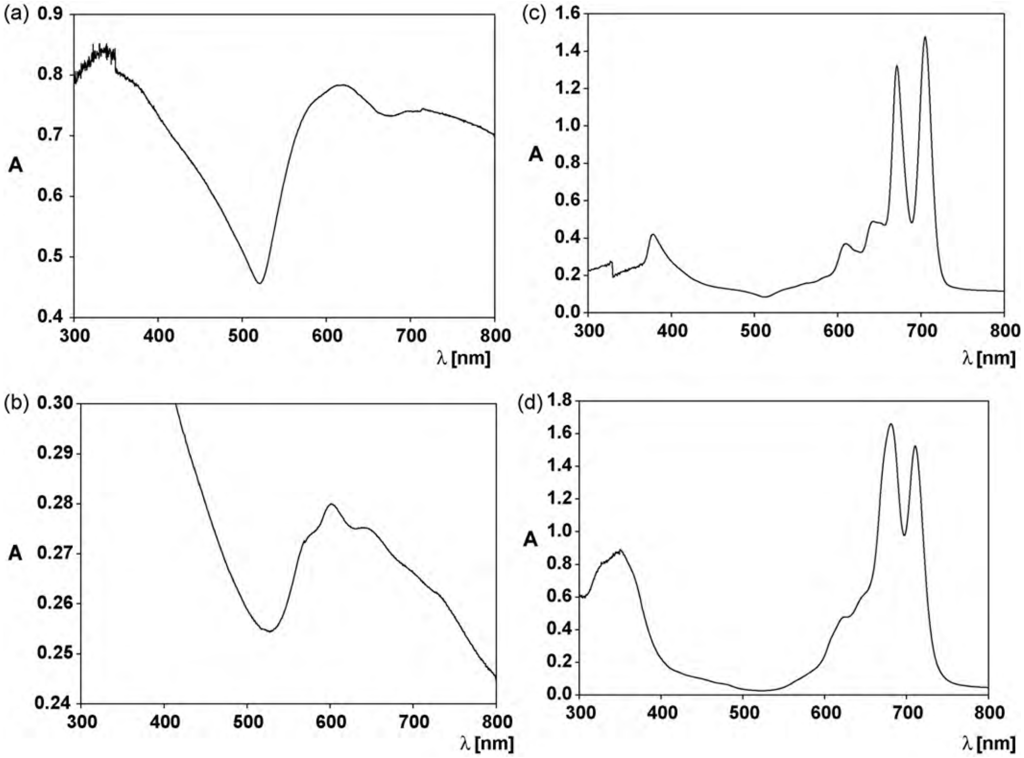

Fig. 4. Comparison of absorption spectra of free phthalocyanine H_2Pc (a – in paraffin oil; c – in quinoline) and demetalizated form of PcYb(OAc) (b – in xerogel; d – in wet gel); in both dotted silica gel probes the TEOS was used as precursor and standard method of dotting, described in Refs. [28,29].

previously described as in ethanol or acetone solution. It is the effect of issue of ethanol and water in poly-condensation reaction. In absolute anhydrous alcohols, the investigated complexes are relatively stable. The sandwich-type complexes are stable in gels, and the demetalization process is observed only for monophthalocyanine complexes.

The aceto-substituted phthalocyanines of lanthanides have several negative properties from the point of view of dotting of silica gels using standard method described above. First of all, the complexes of lanthanides from Ce to Eu have a very weak solubility in most of the organic solvents used for gel dotting. On the other hand, these complexes are demetalized in the presence of light alcohols (such as methanol, ethanol, propanol or izopropanol), which are liberated in time of hydrolysation and poly-condensation of silica gel precursors. But they are relatively stable in butanol. We proposed a new method of transparent monolithic silica gel formed with the use of tetrabutylorthosilicate as precursor. This method is partially based on sol–gel coating method described in the literature [40,41], but in our method we use the hydrochloric acid and water only in trace amounts. The absorption spectra were used to check the encapsulation of the Yb(III) phthalocyanine complex in gel. In the first method of gel synthesis, the complexes are precipitated from gel in the time of drying, as it is shown by the absorption spectra. The precipitation is absent if we use the second method [42], described above. However, in that case we have no ability to observe the dynamics of changes in absorption spectra of investigated complexes in the time of gel formation and drying.

3.2.2. Absorption and emission spectra of Yb(III) phthalocyanine complex encapsulated in gel

The information about attempts of incorporation of monophthalocyanine complexes of lanthanides into silica gels was reported in Ref. [16], but those experiments were not successful enough because of demetalization of complexes in conditions of gel forming reaction. Authors of the paper erroneously described the changes in absorption and emission spectra of lanthanide complexes given by demetalization as dimerization and agglomeration processes [16]. The process of demetalization is easily observed in absorption spectra of probes; the main band of MPc in Q region about 674 nm in wet silica gel was split off in result of molecular symmetry changes (Fig. 4d) and start to be the same as Q band of free phthalocyanine in solution (Fig. 4c). Also in absorption spectrum of xerogel, dotted with PcYb(OAc)it, the shape of bands was almost identical with spectrum of metal-free H_2Pc in paraffin oil, and corresponded to the band of metal-free phthalocyanine on high level of agglomeration, as it is shown in Fig. 4a and b.

Among the aims of this work was implementation of changes in the method of obtaining monolithic transparent silica blocks, dotted with PcYb(OAc). The condition of the experiment should eliminate the demetalization of complexes. The absorption spectra were registered only on initial stages of gel forming process (first method) before the precipitation of investigated complex from gel. The spectra are presented in Fig. 5.

Figs. 6 and 7 display emission spectra of the PcYb(OAc) complex encapsulated in silica gel, using different excitation source (300 and 450 W xenon arc lamp and pulsed Nd-YAG laser). Two regions of the emission spectra were recorded: UV–vis and IR. The UV–vis corresponds to phthalocyanine emission, the second one to $^2F_{5/2}$ state of Yb(III) ion emission.

The emission band of phthalocyanine molecule has low intensity and is more shifted to infrared region than emission bands in solution with the same concentration of the complex (see Fig. 6). The cause of this effect is described earlier as agglomeration of complexes and interactions with silica network [28,29,43].

Metal in phthalocyanine complexes in general exhibits emission from Q band of phthalocyanine macrocycle. The concentration of the macrocycle in silica gel is a bit higher than in starting solution but relatively low, thus self-quenching becomes lesser than in solid state pure complex. Therefore, that emission is well recorded. Although the agglomeration can be observed, it cannot quench

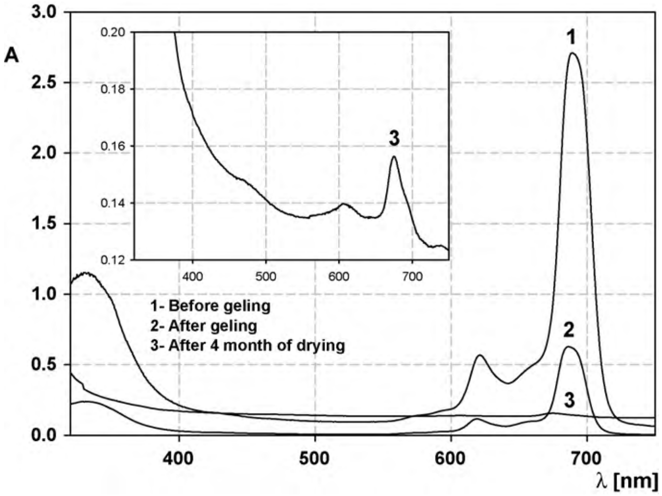

Fig. 5. Absorption spectra of monolithic silica blocks, obtained by sol–gel method with the use of TBOS as precursor, and dotted by PcYb(OAc), on different stages of gel formation. Inset figure: broadened absorption specter of probe after 4 months of drying (plot no. 3 in base figure).

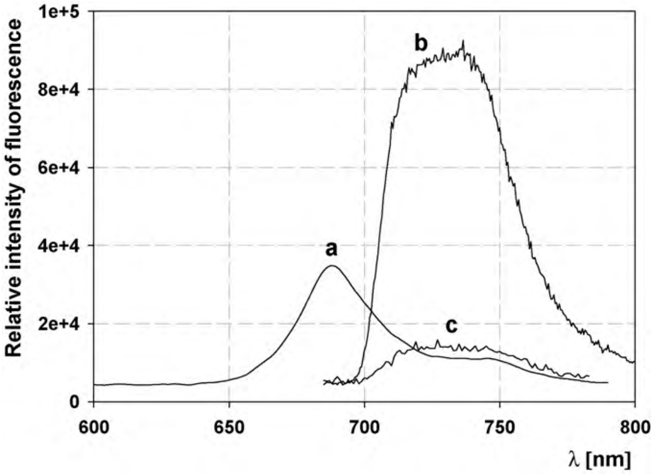

Fig. 6. Emission spectra of PcYb(OAc) in 300 K in DMSO solution with $C_m = 5 \times 10^{-5}$ M (a), $C_m = 5 \times 10^{-4}$ M (b) and in impregnated silica block (c); $\lambda_{exc} = 612$ nm (the 450 W xenon arc lamp was used as excitation source).

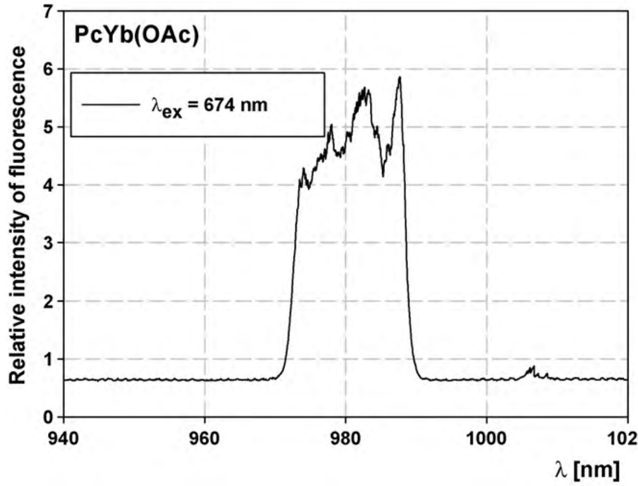

Fig. 7. Emission band of Yb(III) ion in PcYb(OAc) dotted silica gel, obtained by method II in 77 K (the Nd-YAG laser was used as excitation source).

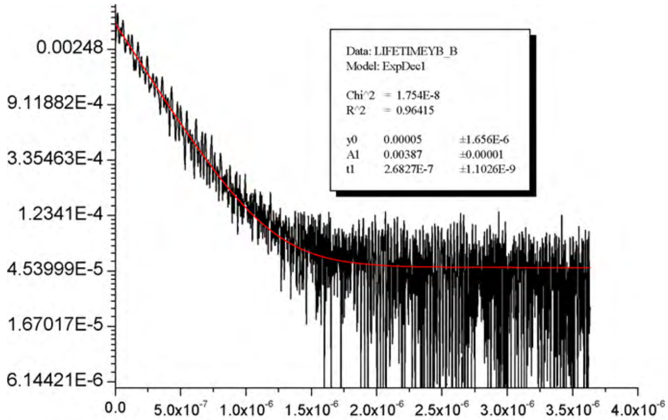

Fig. 8. Luminescence decay curve of the Yb(III) in PcYbOAc complex, entrapped in monolithic silica blocks.

the emission efficiently to this extent. The IR region of the emission spectra shows interior $^2F_{5/2}$ emission. Importantly enough, this emission was excited by 674 nm line, direct through Q band of phthalocyanine. This experiment confirmed good condition for energy transfer from S_1 phthalocyanine state to Yb(III) excited $^2F_{5/2}$ level. Of course, the heavy Yb(III) ion can affect the intersystem crossing (ISC), which can fed the population of the T_1, thus it can also take part in energy transfer. The lifetime decay curve is presented in Fig. 8, and the lifetime of Yb(III) emission is 2.68(1) ms. Although we cannot absolutely eliminate solvent molecules in silica gel, rigidity of the system enhances emission of the Yb(III) ion is sufficiently to observe excellently emission in IR region. Rigidity of the silica gel can also affect the emission in UV–vis region. It is important to note that, when the same conditions of the emission detection were used, the effort to record Yb(III) emission in solid pure PcYb(OAc) complex fails. The reason for this was discussed in the previous paragraph. However, for ytterbium complex in xerogel both emission of phthalocyanine and metal atom were measured.

Since a good standard is needed, a quantum yield of Yb(III) emission in PcYb(OAc) will be published in next paper.

4. Conclusion

The monolithic transparent silica blocks dotted by PcYb(OAc) were obtained. The ligand–metal charge-transfer (LMCT) effect and emission of coordinated Yb(III) ion with excitation on 674 nm (phthalocyanine Q band maximum) in xerogels were reported for the first time.

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References

[1] N.B. McKeown, Phthalocyanine materials: synthesis, in: Structure and Function, Cambridge University Press, New York, 1998.
[2] C.C. Leznoff, A.B.P. Lever, Phthalocyanines: Properties and Applications, VCH, New York, 1996.
[3] K.M. Kadish, K.M. Smith, R. Guilard, The Porphyrin Handbook, vols. 1–10, Academic Press, San Diego, 2001.
[4] J.A. de Saja, M.I. Rodriguez-Méndez, Adv. Colloid Interface Sci. 116 (2005) 1–11.
[5] N. Kobayashi, Coord. Chem. Rev. 227 (2002) 129.
[6] J. Simon, J.J. Adre, Molecular Semiconductors, Springer, Berlin, 1985.
[7] N. Nensala, A. Nzimande, T. Nyokong, J. Photochem. Photobiol. 98 (1996) 129.
[8] D. Wróbel, A. Boguta, J. Photochem. Photobiol. 150 (2002) 67.

[9] N.R. Armstrong, J. Porphyrins Phthalocyanines 4 (2000) 414.
[10] G.A. Kumar, G. Jose, T. Vinoy, N.V. Unnikrishnan, V.P.N. Nampoori, Spectrochim. Acta A 59 (2003) 1.
[11] R.A. Collins, K.A. Mohammed, J. Phys. D 21 (1988) 154.
[12] D. Gu, Q. Chen, X. Tang, G. Fuxi, S. Sten, K. Liu, X. Xu, Thin Solid Films 257 (1995) 88.
[13] (a) J. Sokolnicki, K. Maruszewski, W. Stręk, J. Legendziewicz, J. Sol-Gel Sci. Technol. 11 (1998) 611;
(b) J. Sokolnicki, R. Wiglusz, S. Radzki, A. Graczyk, J. Legendziewicz, Opt. Mater. 26 (2004) 199;
(c) P. Gawryszewska, J. Sokolnicki, J. Legendziewicz, Coord. Chem. Rev. 249 (2005) 2496.
[14] M.A. Villegas, M.A. Garcia, J. Llopis, J.M. Fernandez Navarro, J. Sol-Gel Sci. Technol. 11 (1998) 251.
[15] F. Facca, G. Pucetti, R.M. Leblanc, Colloids Surf. A 149 (1999) 89.
[16] (a) K. Maruszewski, L. Czernicki, W. Wacławek, W. Stręk, J. Mol. Sci. 404 (1997) 141;
(b) J.-C.G. Bünzli, S. Comby, T. Saraidarov, R. Reisfeld, Chem. Phys. Lett. 432 (2006) 128.
[17] (a) V. Bekiari, P. Lianos, P. Judensein, Chem. Phys. Lett. 307 (1999) 310;
(b) K. Binnemans, Chem. Rev. 109 (2009) 4283.
[18] H. Yamashyta, M. Anpo, J. Phys. Chem. B 101 (1997) 10631.
[19] J. Dargiewicz, M. Makarska, St. Radzki, Colloids Surf. A 208 (2002) 159.
[20] P. Battioni, E. Cardin, M. Louloudi, B. Schöllhorn, G.A. Spyroulias, D. Mansuy, T.G. Tailor, Chem. Commun. (1996) 2037.
[21] G. Dubois, R.J.P. Corriu, C. Reyè, S. Brandlés, F. Denat, R. Guilard, Chem. Commun. (1999) 2283.
[22] K.F. Mongey, J.G. Vos, B.D. MacCraith, C.M. McDonagh, Coord. Chem. Rev. 185–186 (1999) 417.
[23] U. Schubert, A. Lorentz, N. Kundo, T. Stuchinskaya, L. Godina, A. Salanov, V. Zaikovskii, V. Maizlish, G.P. Shaposhnikov, Chem. Ber. 130 (1997) 1585.
[24] T. Stuchinskaya, N. Kundo, L. Godina, U. Schubert, A. Lorentz, V. Maizlish, J. Mol. Catal. A: Chem. 140 (1999) 235.
[25] A.B. Sorokin, P. Buisson, A.C. Pierre, Micropor. Mesopor. Mater. 46 (2001) 87.
[26] M. Pędziwiatr, R. Wiglusz, A. Graczyk, J. Legendziewicz, J. Alloys Compd. 451 (2008) 46.
[27] D.K.P. Ng, in: K.A. Gschneidner Jr., L. Eyring, G.H. Lander (Eds.), Handbook on the Physics and Chemistry of Rare Earths, vol. 32, Elsevier Science B.V., Amsterdam, 2001, pp. 611–653 (Chapter 210);
S. Comby, J.-C.G. Bünzli, in: K.A. Gschneidner Jr., J.-C.G. Bünzli, V.K. Pecharsky (Eds.), Handbook on the Physics and Chemistry of Rare Earths, vol. 37, Elsevier Science B.V., Amsterdam, 2007, pp. 217–470 (Chapter 247);
S.H. Bo, J. Hu, Q. Wang, X.H. Liu, Z. Zhen, Photochem. Photobiol. Sci 7 (2008).
[28] Y.S. Gerasymchuk, V.Ya. Chernii, L.A. Tomachynski, J. Legendziewicz, St. Radzki, Opt. Mater. 27 (9) (2005) 1484–1494.
[29] Y.S. Gerasymchuk, PhD Thesis, UMCS, Lublin, 2005 (in Polish).
[30] J. Mack, M.J. Stillman, Coord. Chem. Rev. 219–221 (2001) 993.
[31] M.I. Gayduk, V.V. Grigoryants, A.F. Mironov, V.D. Rumyantseva, V.I. Chissov, G.M. Sukhin, J. Photochem. Photobiol. B: Biol. 7 (1990) 15.
[32] L.A. Martarano, P.C. Wong, W. Horrocks, deW. Jr., A.M.P. Goncalves, J. Phys. Chem. 80 (1976) 2389.
[33] S. Zhuravlyov, N. Rusakova, Yu. Korovin, J. Alloys Compd. 451 (2008) 334.
[34] A. Biednarkiewicz, Z. Drullis-Kawa, R. Wiglusz, J. Legendziewicz, Proc. SPIE 586 (3) (2005) 152.
[35] A. Biednarkiewicz, R. Wiglusz, J. Legendziewicz, W Stręk, Polish Patent PL375718, 2006.
[36] R. Weiss, J. Fisher, Lanthanide phthalocyanine complexes, in: K.M. Kadish, K.M. Smith, R. Guilard (Eds.), The Porphyrin Handbook, vol. 16, Elsevier Science, 2003.
[37] P. Godlewska, Y.S. Gerasymchuk, L.A. Tomachynskii, J. Legendziewicz, J. Hanuza, J. Struct. Chem. 21 (2) (2010) 461.
[38] (a) G. Socrates, Infrared and Raman Characteristic Group Frequencies, J. Wiley and Sons, Ltd., Chichester, 2001;
(b) V. Nemykin, A. Tsivadze, N. Subbotin, N. Kostromina, S. Volkov, Koordinatsyonnaya Khimiya 22 (4) (1996) 315 (in Russian).
[39] (a) J. Janczak, I.M. Idemori, Polyhedron 22 (2003) 1167;
(b) R. Kubiak, J. Janczak, J. Mol. Struct. 935 (2009) 53.
[40] S. Inazawa, K. Yamada, K. Sawada, European Patent EP0416131, 1994.
[41] K. Kang, H. Rhee, Micropor. Mesopor. Mater. 84 (2005) 34.
[42] T. Sergio, Fujiwara, Yoshitaka Gushikem, J. Braz. Chem. Soc. 10 (5) (1999) 389.
[43] (a) R. Litrán, E. Blanco, M. Ramirez-del-Solar, J. Non-Cryst. Solids 333 (2004) 327;
(b) Z. Hongbing, Ch. Wenzhe, L. Guanghui, W. Minquan, Mater. Sci. Eng. B 100 (2003) 113;
(c) Z. Hongbing, Ch. Wenzhe, W. Minquan, Mater. Lett. 57 (2003) 1108;
(d) Z. Hongbing, Ch. Wenzhe, Ch. Jianchun, W. Minquan, Mater. Sci. Eng. B 100 (2003) 119.