

Luminescence properties of a Nd(III) coumarin derivative complex immobilized in a poly(methylmethacrylate) matrix

M. GETSOVA, V. KIRCHEVA, J. ZAHARIEVA, I. MANOLOV^a, H. NARUKE^b, M. MILANOVA^{*}

Sofia University, Faculty of Chemistry, Department of Inorganic Chemistry, 1, J. Bourchier, 1164 Sofia, Bulgaria

^a*Medical University, Faculty of Pharmacy, Department of Organic Chemistry, 2, Dunav Str., 1000 Sofia, Bulgaria*

^b*Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan*

A complex of Nd(III) with 3,3'-[(4-chlorophenyl)methylene]bis-(4-hydroxy-2H-1-benzopyran-2-one) (symbol L15) was immobilized in poly(methylmethacrylate) (PMMA) films and the properties of the composites obtained were studied. The films contained 1 wt. % of the complex and were deposited by spin- and dip-coating techniques. The IR spectroscopy data prove the presence of the complex in the films. The morphology of the pure films and those containing the complex was investigated by scanning electron microscopy, transmission electron microscopy and atomic force microscopy. In order to understand the photoluminescent properties of nanocomposite films with Nd(III), the emission spectra were recorded and discussed. The immobilization of the complex in films does not disturb its optical properties. The morphology and the luminescent properties of the immobilized complexes indicate that they may be used for active components in optical devices.

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1. Introduction

The application of lanthanoids, Ln(III), as key components of optical materials, LED/OLED devices and solar energy converters has been the subject of many publications [1-3]. Many of the applications of Ln(III) are determined by the properties of their coordination compounds with ligands such as beta-diketones [4,5] and porphyrins [6]. Some complexes of Yb(III), Er(III) and Nd(III) have found application because of their NIR-luminescence activity [7]. For sensitization of Ln(III) luminescence in NIR some chromophoric dyes including coumarin have been mentioned [1]. In spite of the fact that the NIR emission of Ln has been explored in bio-imaging [8,9] and optical electroluminescent materials [9], it is still interesting to look for new Ln(III) optical materials with wide applications. Recently in our group complexes of Ln(III) with biscoumarin derivatives, possessing different substitutes were synthesized and characterized and interesting properties were found. On their base we have been looking for preparation of materials with optical properties *via* immobilization of the Ln biscoumarin complexes in polymeric matrices.

1.1. Coumarins

The benzo- α -pyrones, or coumarins, are a group of compounds consisting of fused pyrone and benzene rings, with the pyrone carbonyl group at position 2 (IUPAC name 2H-chromen-2-one, and also known as 1-benzopyran-2-one) [10]. Recently, coumarin derivatives

have attracted scientific interest because of the interesting properties these compounds possess, namely bioactivity and physiological properties [11-14]; their optical properties allow applications as laser dyes, phosphorescent [17] and photochemical materials [16, 17] as well as probes for heterogeneous systems using fluorescence spectroscopy [10].

The coumarins used in our ongoing research, partially presented here, belong to a group of so called bis-coumarins that are derivatives of 3,3'-benzylidene-bis(4-hydroxy-2H-1-benzopyran-2-one), possessing substitutes like -OH, -NO₂, -OCH₃, -Cl etc. Our experiments show that the substitute influences the properties of the respective coumarin. The coumarin derivative 3,3'-[(4-chlorophenyl)methylene]-bis(4-hydroxy-2H-1-benzopyran-2-one), (L15), (Fig. 1), possessing a -Cl substitute on the para position, was used in the research presented here.

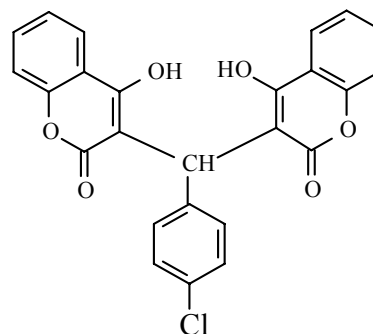


Fig. 1. Formula of L15.

1.2. Ln(III) -complexes with coumarins

The synthesis of complexes of La(III), Ce(III) and Nd(III) with 3,3'-benzylidene-bis(4-hydroxy-2H-1-benzopyran-2-one) [18-21] as well as of Ce(III), Nd(III) [22] and Pr(III) [23] with coumarin-3-carboxylic acid has been reported and their spectral properties have been characterized. The crystal structure of complexes of coumarin derivatives with Pr(III), Eu(III), Gd(III), Tb(III) and Er(III) has been investigated and the effect of the lanthanide radii on the structure and on the photoluminescence properties has been studied [24]. It has been found that both the biological [25, 26] and optical [20] properties of the coumarins are improved after coordination with different metal ions, including with Ln(III) ions.

1.3. Immobilization of Ln complexes

Considering their relatively low stability and plasticity, lanthanide complexes usually have been applied through introducing them into matrices [27]. According to [2, 28-30], the thermal stability and the luminescence properties of Ln(III) complexes are improved when immobilized in matrices. Different matrices for immobilization have been investigated. Among them silica sol-gel glasses have shown disadvantages because of the quenching of the excited states of the lanthanide ions *via* vibronic coupling with the hydroxyl group vibrations (in Si-OH and H₂O) [31]. A matrix of poly(methylmethacrylate) (PMMA) is often used. PMMA is a light weight, colorless material and possesses properties such as high transparency, light transmittance, excellent UV stability, chemical and thermal resistance and a good solubility in many organic solvents. It has been found that a PMMA matrix can act as a co-sensitizer and enhance the luminescence intensity of the films [32]. At the same time it provides considerable UV protection for the luminescent species and improves the photostability of the doped complexes.

PMMA-based composites have been produced both by using a chloroform solution of the polymer or by performing the polymerization of the monomer methylmethacrylate (MMA) using an initiator such as benzoyl peroxide (BPO) in the presence of the complex for immobilization [33]. The latter method was applied for the preparation of a Eu(TTA)₃.Phen-containing composite from dimethylformamide (DMF) solutions of the complex. The polymerization process took place at 80-90 °C for 15 - 30 min, and was completed at 50 °C for 24 h. An analogous preparation method has been employed for ethylmethacrylate [34]. The PMMA has been used for immobilization of complexes of Tb(III) [35], Eu(III) [36] and Nd(III) [37] as well as for a co-ligand to coordinate to Ln(III) ions [38]. The Ln(III) doped polymeric materials have a number of possible applications in optical devices [39, 40], in particular Nd(III) in waveguide amplifiers and laser applications [34].

1.4. Contribution of the present work

1.4.1. PMMA matrices are studied applying both synthetic techniques, namely dissolution of the complex into the monomer solution followed by polymerization or dissolving the polymer and the complex in a cosolvent and evaporation of the latter.

1.4.2. The Nd(III) complex with the coumarin derivative 3,3'-[(4-chlorophenyl)methylene]bis(4-hydroxy-2H-1-benzopyran-2-one) is immobilized in PMMA matrices in an attempt to expand the application of this kind of complexes.

1.4.3. The morphology of the prepared films as well as the influence of the immobilization of the complex on its optical properties are studied, thus helping the evaluation of their applicability as active components of optical devices.

2. Experimental

2.1. Materials

Methylmethacrylate monomer (CH₂:C(CH₃)COOCH₃, MMA), Nd(NO₃)₃.6H₂O, (> 99.95%) and N, N-dimethylformamide (HCON(CH₃)₂, DMF), (> 99.5%) were purchased from Kanto Chemical. Benzoyl peroxide (C₁₄H₁₀O₄, BPO) (75%) was purchased from Acros Organics. Poly(methylmethacrylate) ((C₅O₂H₈)_n, PMMA), M=90 000 and chloroform, CHCl₃, were obtained from Sigma Aldrich. The synthesis and the characterization of the neodymium complex used here (symbol NdL15) will be described in a separate publication. Elemental analysis suggests the molecular formula Nd(OH)L15.H₂O, while molecular weight analysis of a similar complex suggests that they form oligomers containing 2-4 rare earth ions. The complex does not crystallise, so XRD does not yield information on its structure. Glass microscope slides, cleaned sequentially with deionized water, methanol, acetone and again deionized water, were used as film substrates.

2.2. Film preparation procedure.

2.2.1. *by in situ polymerization of MMA using BPO*

A dimethylformamide (DMF) solution of the neodymium coumarin complex NdL15 (3.0 ml, 2.2 wt. %) was mixed with methylmethacrylate, MMA, (4.0 ml) to obtain a dopant concentration of 1 wt. %. Then benzoyl peroxide (BPO) (0.009 g.) was added to the mixed solution as a catalyst for MMA polymerization. The mixture obtained was placed in a water bath at 80°C for 90 min under magnetic stirring. After the pre-polymerization of the monomer, the mixture became viscous.

Films were deposited by spin coating of 0.5 ml of viscous solution using a Vacuum Spin Coater (Imoto Machinery) at 3000 rpm, with a spinning time of 30 sec (these were found to be optimal conditions).

The bulk materials were prepared by casting the viscous solution in a small glass vessel with a flat bottom

surface. The vessel with the sample was left to dry in a drying stove in static air at 65 °C. Later the material was removed from the vessel.

The polymerization of the films and the matrices were completed at 65 °C for 72 h in static air in a drying stove. In parallel, films and bulk material were prepared without coumarin complex as well.

2.2.2. from PMMA solution in chloroform

A solution of NdL15 in DMF (4.0 ml, 2.2 wt. %) was mixed with a solution of PMMA in CHCl₃ (10.0 ml, 25 wt. %) in order to obtain a concentration of the dopant NdL15 of 1 wt. %. Films were produced on glass substrate by dip coating using a withdrawal speed of 0.4 mm/s (this was found to be the optimal speed).

2.3. Methods for characterization

Infrared spectroscopy: Infrared spectral analysis was carried out on a JASCO FTIR-410 spectrometer. Absorption spectra were measured from 4000 to 400 cm⁻¹ using KBr pellets. The resolution was 4 cm⁻¹ for all recorded spectra.

Scanning electron microscopy (JEOL) and field emission scanning electron microscopy (Hitachi S-5200 FE-SEM, 30 kV) were used to analyze the morphology of the thin films.

Transmission electron microscopy: a JEOL JEM 2100 HRTEM, 200 kV, magnification up to 1 500 000 times was used. The films were exposed to the action of HF vapors for 10 s and were removed from the glass substrate after soaking in water. The films were fixed on a standard Cu substrate for TEM observation and dried at room temperature. Particle size distributions were estimated by analyzing TEM images with the ImageJ software package.

Atomic Force Microscopy: Veeco MultiMode and Agilent 5500 microscopes were used for observing the morphology of the films.

Fluorescence spectrometry: a NQ21A0028 spectrometer with a diode pumped solid state (DPSS) Nd:YAG laser with 532 nm wavelength laser pointer (continuous wave (CW) irradiation, initial power 42 mW) was used.

UV-VIS absorption spectroscopy: an Evolution 300 UV-Vis spectrometer (Thermo Scientific) was used for measuring the absorption of the samples in the range 200-900 nm,

3. Results and discussion

3.1. Immobilization by in situ polymerization of MMA matrix using BPO.

3.1.1. Presence of NdL15 in the composite

IR spectra of a powder of the NdL15 complex, of NdL15 complex-containing PMMA as well as of pure PMMA obtained by the same procedure are shown in the

wavelength range 2000-400 cm⁻¹ in Fig.2a and 4000-2000 cm⁻¹ in Fig.2b, respectively.

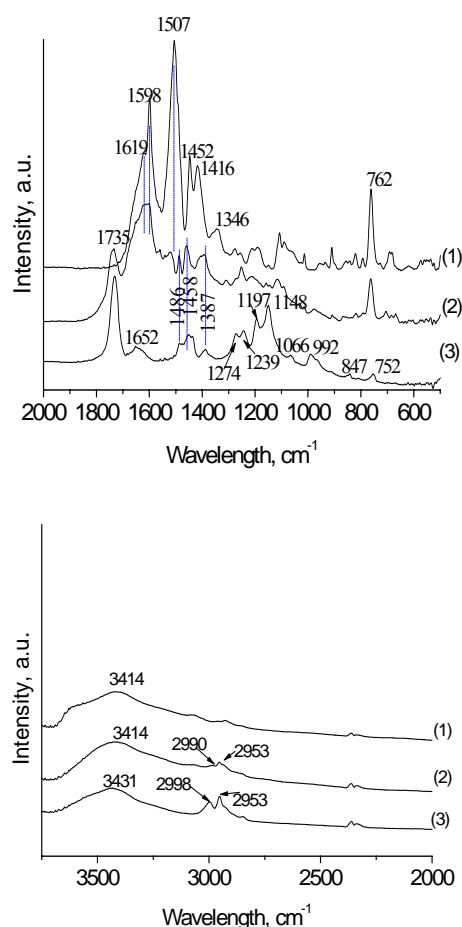


Fig. 2. IR spectra of pure NdL15 (1), of NdL15/PMMA (2), and of pure PMMA obtained by the same procedure (3) at room temperature in the wavelength range 2000 - 400 cm⁻¹ (a) and 4000 - 2000 cm⁻¹ (b), from top to bottom.

- **Pure PMMA:** the IR spectrum of the pure PMMA (Fig.2a, 3) shows an intensive narrow absorption peak at 1733 cm⁻¹ due to the free carbonyl C=O stretching band of an acrylate group, present in the unconjugated ester, which is typical for both MMA and PMMA. The ester group O-CH₃ in PMMA is characterized by the band at 1486 cm⁻¹. The absorption bands between 1150 and 1280 cm⁻¹ (1148, 1197, 1239 and 1274 cm⁻¹) can be attributed to the C-O-C stretching vibrations. The weak absorption at 1387 cm⁻¹ can be ascribed to the methyl group deformation band, and the one at 752 cm⁻¹ can be attributed to the methyl rocking mode. The band at 1455 cm⁻¹ can be ascribed to the bending vibration of the C-H bonds of the -CH₃ group. The two bands at 2998 cm⁻¹ and 2953 cm⁻¹ can be assigned to the C-H bond stretching vibrations of the -CH₃ and -CH₂- groups, respectively (Fig.2, b, 3). The data are in agreement with the literature data [41, 42]. In addition, there are two weak broad absorption bands at 3431 cm⁻¹ and 1652 cm⁻¹, which can be attributed to the -OH group stretching and bending vibrations, respectively, of

physisorbed moisture [43]. According to [42], the bands at 992 cm^{-1} together with the bands at 1066 cm^{-1} and 847 cm^{-1} are the characteristic absorption vibrations of PMMA; their presence proves that polymerization to PMMA was successful.

- *NdL15 complex in a PMMA matrix*: in the IR spectrum of the pure NdL15 complex (Fig. 2a, 1) the very sharp strong band at 1598 cm^{-1} can be ascribed to the $\nu_{\text{sym}}(\text{C}=\text{O})$ of the carbonyl group responsible for Nd(III) ion coordination. This is the most informative band indicating the presence or formation of the complex. The intensity of this band slightly decreased for the NdL15 immobilized in PMMA matrix (Fig. 2a, 2), which can be explained with the low complex concentration in PMMA matrix (1 wt. %). It appeared at 1602 cm^{-1} . The shoulder at 1619 cm^{-1} , ascribed to the asymmetric vibration of the carbonyl group $\nu_{\text{asym}}(\text{C}=\text{O})$ [19, 20] coordinated to a Ln(III) ion, is observed in the pure NdL15 as well as in the NdL15/PMMA composite (Fig. 2a, 2). The intensity of some other characteristic bands in the IR spectrum of the NdL15 complex is influenced by its low concentration in the PMMA matrix. The absorption band at 1507 cm^{-1} due to the stretching vibrations of the carbon-carbon bonds $\nu(\text{CC})$ and deformation vibrations $\delta(\text{CCH})$ in plane of the coumarin rings of the complex are in accordance with the statement in [19, 20]. The latter have lower intensity in the NdL15/PMMA composite in comparison with the pure NdL15. The very well expressed vibration bands at 1452 and 1416 cm^{-1} in the spectrum of the pure NdL15 (Fig.2a, 1) also show a decreased intensity after the immobilization of the complex (Fig.2a, 2). The main influence of the PMMA matrix on the IR spectrum of the complex is the decreased intensity of bands which are characteristic for NdL15. There is neither shifting of the position nor broadening of the bands of NdL15.

As can be expected, the characteristic PMMA bands mentioned above are present in the spectrum of NdL15/PMMA composite as well, with a somewhat lower intensity (Fig.2a, 2).

3.1.2. NdL15/PMMA film morphology

Using both the spin and dip coating techniques, very smooth thin films were obtained on glass substrate. The smoothness of the films is rather similar for dip and spin coating, but their thickness is different as can be seen from the cross section SEM images (Fig.3). The thicker films are obtained by spin ($5\text{--}7\text{ }\mu\text{m}$) compared with dip ($2\text{--}3\text{ }\mu\text{m}$) coating. This tendency is in agreement with the results we got using these coating techniques to prepare SiO_2 -based films [44]. Only one dipping or spinning step was applied here because the number of immersions increases the thickness [44] and this makes it more difficult for analytes such as oxygen to reach the immobilized complex when the films are used in analytical sensors.

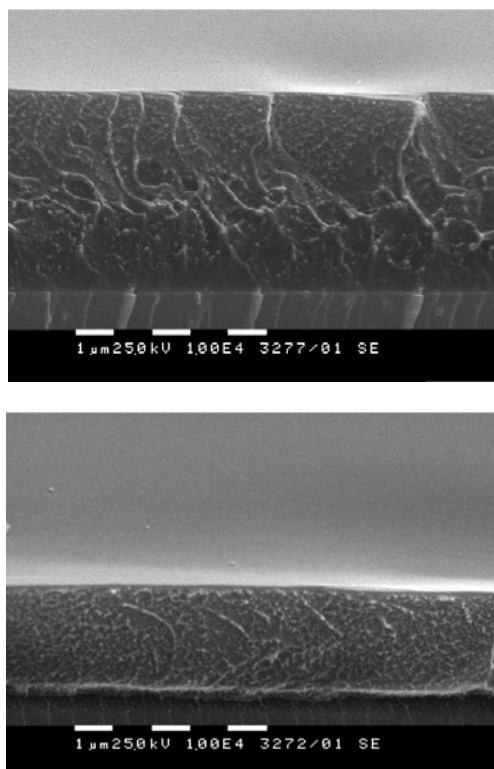


Fig. 3. SEM images of cross section of NdL15/PMMA films deposited by spin- and dip coating (from top to bottom).

The SEM images of films with different magnifications are shown in Fig. 4, where small grains are observed only at an enlargement of 50 000.

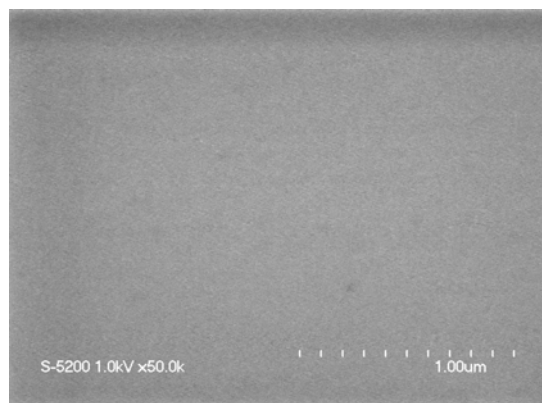


Fig. 4. SEM image of film of NdL15/PMMA composite deposited on glass substrate at amplification $\times 50\,000$.

The grain size of the films produced by dip-coating, estimated from the TEM images, is in the range of $0.5\text{--}1\text{ nm}$ (Fig. 5). The largest number of particles are in the $0.8\text{--}0.85\text{ nm}$ size range.

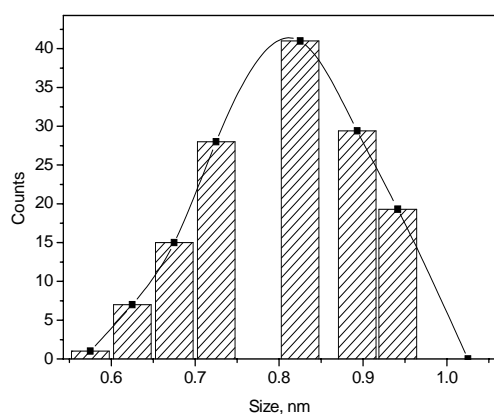


Fig. 5. Particle size distribution of the films prepared by dip coating. The largest number of particles are in the 0.8-0.85 nm size range.

Comparing the TEM images of pure PMMA (Fig. 6a), and NdL15/PMMA, *in situ* polymerization (Fig. 6b) small differences in the morphology of the films are apparent. In the pure MMA based polymeric film (Fig. 6a), wave-like formations are observed. Very well-distributed grains on the surface of the MMA-based NdL15 -containing polymeric film are visible (Fig. 6b).

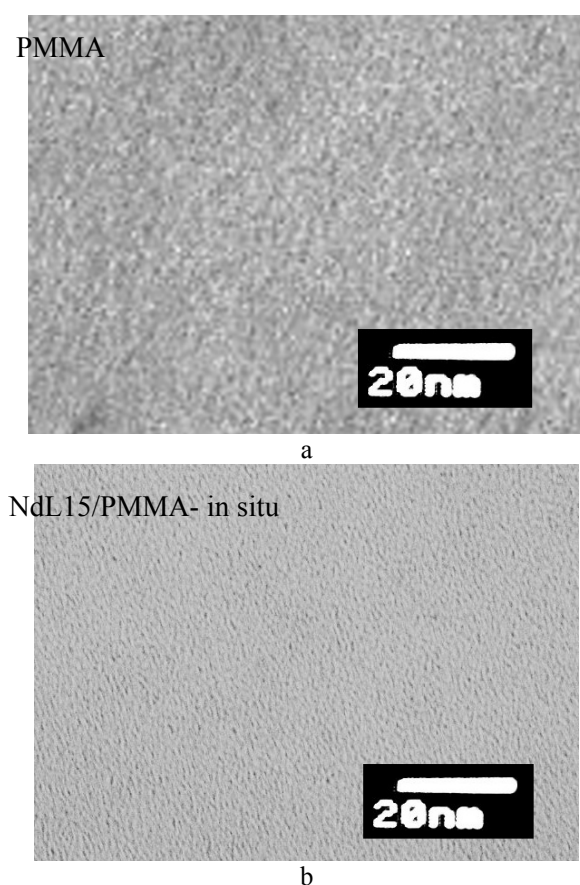


Fig. 6. TEM images of films produced by dip-coating from solutions based on pure PMMA (a), and NdL15/PMMA, *in situ* polymerization (b) from top to bottom.

A smooth surface with small homogeneously distributed grains can also be seen in the AFM images in Fig. 7.

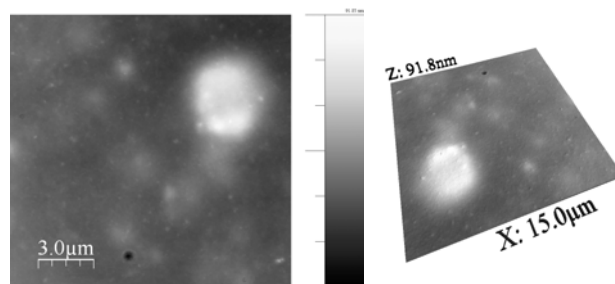


Fig. 7. AFM image of NdL15/PMMA, *in situ* polymerization based film

3.2. Immobilization in PMMA/chloroform solution

Films of PMMA with immobilized NdL15: The IR spectrum (Fig. 8) shows characteristic absorption bands of the pure matrix and the NdL15 complex. The concentration of the dopant was kept at 1 wt. % because any attempt to increase the NdL15 concentration lead to the formation of opaque films after drying. This could be due to the NdL15 somehow disturbing the formation of the film. The same opaque films were observed in an attempt to obtain a film using a sodium salt of the ligand, NaL15, dissolved in dimethylsulfoxide (DMSO). In the absence of the complex or any other salt the PMMA/CHCl₃ sol gives a transparent film.

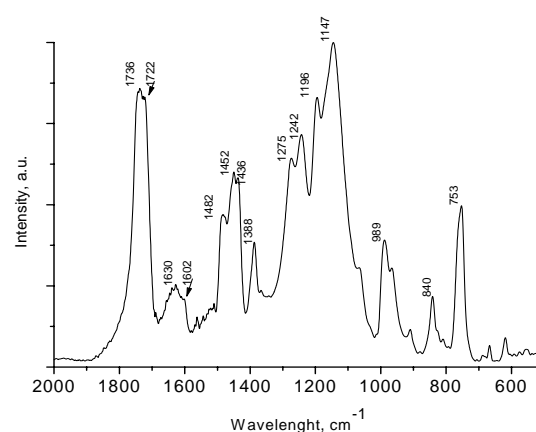


Fig. 8. IR spectrum of NdL15/PMMA/CH₃Cl.

The morphology of the surface was investigated by AFM by scanning areas of 15x15 μm as well as 1x1 μm. The AFM image of the NdL15/PMMA/CHCl₃ composite film (15 x 15 μm) with section analysis at different spots on the surface is shown in Fig. 9. Pores with a large size distribution can be seen (Fig. 9). They are quite likely a result of the evaporation of the solvent from the matrix during the polymerization process. The size of the pores

visible on the surface varies; some of them are very small (typically $0.1 \times 0.2 \mu\text{m}$), others are $1 \times 2 \mu\text{m}$ or even bigger. The depth of the pores varies between $0.2 - 2 \mu\text{m}$ (Fig. 9). The film thickness and especially the size of the pores are of importance for the potential application of the films in optical analytical sensors where the analyte should be accessible to the immobilized fluorescent complex. MMA/NdL15 films prepared by *in situ* polymerization appeared smooth and homogeneous and such big pores were not observed (Fig. 7).

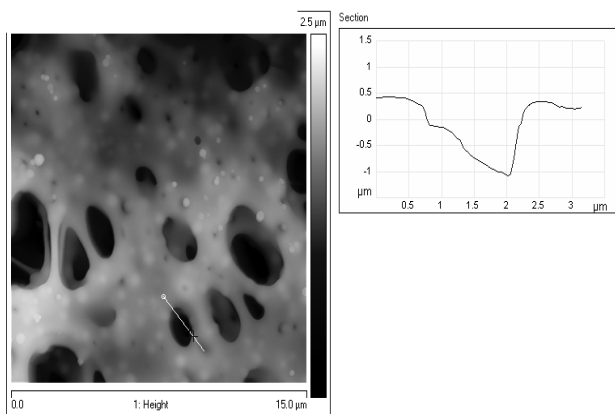


Fig. 9. AFM image ($15 \times 15 \mu\text{m}$) of the NdL15/PMMA/ CHCl_3 composite film with section analysis at different spots on the surface.

Scanning a $1 \times 1 \mu\text{m}$ area of the surface in more detail (Fig.10) shows grain-like formations that cannot be noticed on the $15 \times 15 \mu\text{m}$ image. The grains are between 1-2 nm in size. The height of the grain-like formations is not more than 2-3 nm, looking at the scale of the image (Fig. 10) $1 \times 1 \mu\text{m} \times 4 \text{ nm}$. Grains are observed by TEM as well (Fig. 11). The grains are likely to be associated with the NdL15 complex. X-ray diffraction analysis of a single crystal of a similar bis-coumarin (the only difference being the -Cl substitue being replace by -OH) resulted in a volume of the unit cell of approx. 1 nm^3 . The volume of the grains seen in Fig. 10 are of a similar order of magnitude and may thus be oligomers of 2-4 NdL15 units.

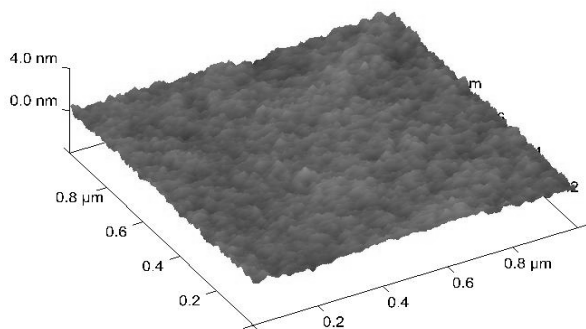


Fig. 10. AFM image ($1 \times 1 \mu\text{m}$) of NdL15/PMMA/ CH_3Cl .

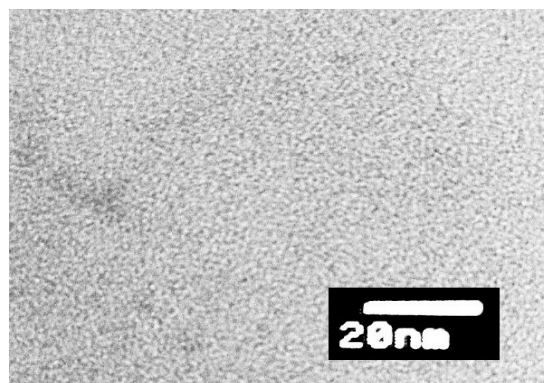


Fig. 11. TEM image of NdL15/PMMA/ CH_3Cl film

3.3. Optical properties of the films produced

The films obtained showed strong absorbance in the UV range (Fig. 12) with a maximum around 300 nm and a good transmittance in the range above 400 nm.

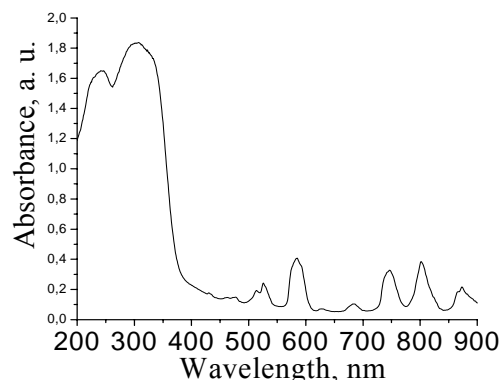


Fig. 12. Absorption of NdL15/PMMA/ CH_3Cl in the range 200-900 nm.

The characteristic NIR luminescent emission of the Nd (III) ion was observed in the region 850-1100 nm (Fig.13) at an excitation wavelength of 532 nm. The very high intensity band at 1074 nm due to the transition ${}^4\text{F}_{3/2} \rightarrow {}^4\text{I}_{11/2}$ is seen in the spectrum of pure NdL15 (Fig.13, (3)), as well as in the spectra of the two different NdL15/PMMA composites (Fig.13, (1) and (2)). This main fluorescence line is used for application in Nd:YAG lasers [1] and amplifiers [27]. Usually a somewhat shorter wavelength of 1065 nm [1, 27] is observed than the wavelength observed in our case (1074 nm). Relatively weak signals of singlets, doublets and triplets were observed in the spectrum of the pure complex as well as in the spectra of the films. The bands at 1026, 1037 and 1049 nm can be considered as splitting of the line of the transition ${}^4\text{F}_{3/2} \rightarrow {}^4\text{I}_{11/2}$ into bands of unequal intensity. A similar splitting of the band of that transition to multiplet has been observed in [27] as well. However, the ratio of the intensities of the multiplet observed there is different than that here. The very weak band at 980 nm can be ascribed to the transition ${}^4\text{F}_{3/2} \rightarrow {}^4\text{I}_{9/2}$ and the doublet (1384, 1404 nm) to the transition ${}^4\text{F}_{3/2} \rightarrow {}^4\text{I}_{13/2}$ [1,2,4]. The transition ${}^4\text{F}_{3/2} \rightarrow {}^4\text{I}_{13/2}$ is well known to be within the range

of a telecommunication window [1]. Unfortunately in our case it is not very intensive. The lack of quenching of the luminescence intensity of the complex and the very strong intensity of the main line at 1074 nm makes the PMMA matrix very suitable for oxygen sensing applications. The influence of oxygen on the luminescence of the complex can be tested in the future without interference of the matrix.

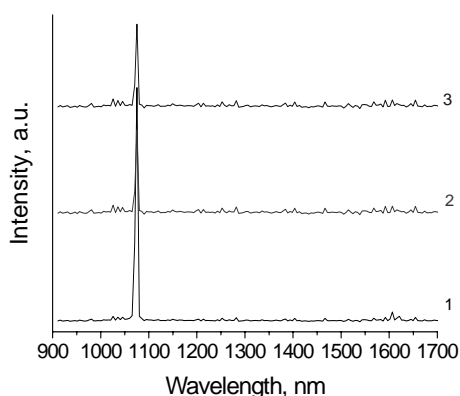


Fig.13 Emission spectra of NdL15/PMMA composite film (1), NdL15/PMMA in situ polymerization (2), and pure NdL15 (3), excitation with Nd:YAG at 532 nm.

4. Conclusion

Luminescent materials consisting of a Nd(III) coumarin complex immobilized in a PMMA matrix were prepared in order to extend the application of this complex in NIR optics. The synthetic procedure is simple and easily reproducible. The *in situ* polymerization of MMA in the presence of Nd(III) coumarin complex was successful using BPO as an initiator. By this procedure smooth and homogeneous films can be produced. The morphology of the composites NdL15/PMMA was investigated in order to find some characteristics with potential influence on the properties of NdL15. The immobilization of the complex in a PMMA film does not disturb its molecular structure and optical properties. The PMMA films with immobilized Nd(III) coumarin complex have shown properties such as fluorescence in the NIR region that can be useful for practical application. For now the strong emission of the NdL15 observed when immobilized in the composites is rather promising. The main question about the way the NdL15 is embedded in the matrix is not yet resolved.

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*Corresponding author: nhmm@wmail.chem.uni-sofia.bg,