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Luminescence properties of chitosan doped with europium complex

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ABSTRACT

Chitosan is a natural, biodegradable and biocompatible polymer. It is transparent in UV–vis region. Nonetheless, appropriate doping may significantly change its optical properties. Chitosan film doped with Eu^{+3} β-diketonate complex was synthesized. Absorption, photoluminescence and time resolved decay properties of this material were investigated. It is shown, that the material exhibits excellent luminescence emission in VIS region with high quantum efficiency of approximately 47%. These exceptional properties allow for various applications of this material. In particular, it provides a good basis for the construction of biocompatible luminescent sensor.

1. Introduction

In recent decades an increasing interest was observed on synthesis of lanthanides complexes possessing high quantum efficiencies in water environment. This trend of studies is developed by various applications of luminescent lanthanide probes for time-resolved immunoassays, time-resolved luminescent microscopy and optical sensors of pH, oxygen pressure, temperature and selected anions. Doping such complexes in biocompatible materials may be considered as alternative way to construct highly efficient luminescent systems for bio analytical applications [1–3].

Synthetic UV transparent polymers, especially poly(methyl methacrylate) (PMMA) doped by luminescence lanthanide complexes has been widely investigated [4]. On the other hand the complexes were introduced also to various hole transport polymers such as poly (N-vinylcarbazole) (PVK), poly[2-methoxy-5-(2′-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV), and others to investigate mainly organic light emitting diodes (OLEDs) [5]. Luminescence quantum efficiency of Eu $^5D_0 \rightarrow {}^7F_J$ ($J=0, 1,\ldots,4$) luminescence is high even at room temperature (0.33 and 0.71 in toluene and PMMA films, respectively) [6]. This property is important for practical applications. The environmental requirements for safety and recyclability extorts to combine these functional materials with low cost, environmentally friendly biopolymers to synthesize hybrid materials. Natural, biodegradable and biocompatible chitosan produced from crab shells or shrimps is a promising candidate, as a matrix material, for various optical applications. This low cost produced polysaccharide has many interesting properties e.g. ability to form films, non-toxicity, excellent adsorption features etc. which makes it excellent to prepare functional hybrid materials [7]. Chitosan is used to prepare hydrogels, films, fibers or sponges in the biomedical domain, for which the biocompatilibity is essential. It is widely applied e.g. in medicine, pharmacy, cosmetics and agriculture because it exhibits antivirus and antiphage activities as well in bone tissue engineering etc. [8,9].

Chitosan nanoparticles, thin films and membranes seem to be particularly interesting for various applications. Chitosan nanoparticles doped with trivalent lanthanide ions could found medical application as fluorescent labels [10]. Composite materials based on PMMA thin films doped with europium complexes may be applied as UV radiation converters [6]. Pure chitosan film is transparent for UV–vis light [11] and may be used as a matrix for various chemical compounds. Therefore this polymer can be applied as a biocompatible sensor as well. This work presents luminescence properties of chitosan doped with Eu^{3+} fluorinated β-diketone (TTA) complex.

2. Experiment

Chitosan is a natural polymer of acetylamino-α-glucose. A structural formula of chitosan is depicted in Fig. 1a. The investigated europium complex $Eu(TTA)_3DAPM$, (TTA—thenoyltrifluoroacetone, DAPM—diantipyrylpropylmethane) is shown in Fig. 1b. The ligand DAPM saturates coordination number of Eu ion stabilizing structure of $Eu(TTA)_3DAPM$. As a consequence, it improves luminescence properties of the investigated complex.

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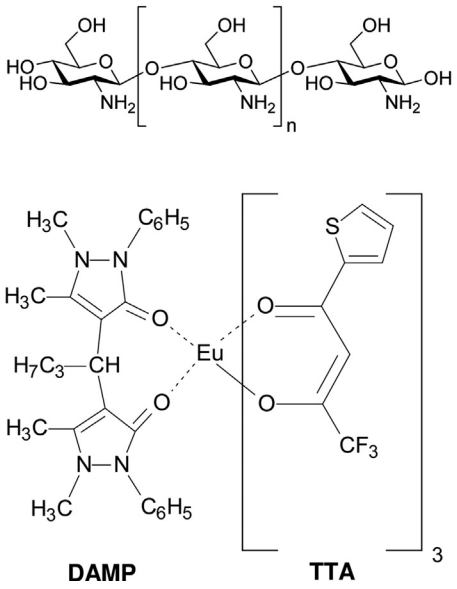

Fig. 1. Chemical structure of (a) chitosan and (b) $Eu(TTA)_3DAPM$ complex.

The chitosan used for sample preparation was purchased from the Institute of Sea Fisheries in Gdynia (Poland). The deacetylation and viscosity of this chitosan were 73% and 256 mPa s, respectively. The 0.75 g of dry chitosan was dissolved in 85 mL (1%) acetic acid in distilled water. Solution of $Eu(TTA)_3DAPH$ was prepared by dissolving 30 mg of $Eu(TTA)_3DAPH$ in 10 mL of methanol. Then, the solutions of acetate chitosan and $Eu(TTA)_3DAPH$ in methanol were mixed in proper amounts to obtain 5.45% weight of europium complex relative to chitosan mass. Final solution was deposited at smooth poly(methyl methacrylate) (PMMA) or glass surfaces and dried for 24 h at 313 K. The obtained layers were homogeneous and transparent. Thickness of the layers was in the range 5–100 μm, depending on the amount of deposited solution. Absorption spectra were measured using Schimadzu spectrophotometer UV-240PC at wavelength range 230–400 nm with resolution of 0.1 nm, in air, at room temperature.

Photoluminescence (PL) measurements were carried out in vacuum at 80.5 K, after excitation by 350 nm light using 75 W Xenon arc lamp. More details of the measurement equipment are given in some earlier papers [12,13]. Wavelength resolution of PL measurements was 0.3 nm. Finally, numerical calibration of photoluminescence spectra was done taking into account sensitivity of the whole measurement system.

Time-resolved measurements of luminescence excitation and emission spectra as well as decay kinetics were carried out using spectrofluorimeter FLUORAT-02-PANORAMA LUMEX. The light source was a high pressure flash Xe-lamp. It operates with 1 μs pulse and repetition frequency of 25 Hz. Emission of luminescence may be detected in spectrum range 210–730 nm with resolution of 15 nm. The measurements were carried out in ambient conditions. The delay and duration times were adjusted to investigated samples.

3. Results

Absorption spectra of TTA,DAPM $Eu(TTA)_3 \cdot DAPM$ in methanol solution and $Eu(TTA)_3DAPM$ (5.45%) in chitosan film are shown in Fig. 2. Absorption peaks of TTA (337 nm) and DAPM ligands (276 nm) in methanol solution correspond to peaks obtained for $Eu(TTA)_3DAPM$ in methanol solution (336 nm and 283 nm) and europium-chitosan film (355 nm and 291 nm). Absorption peaks

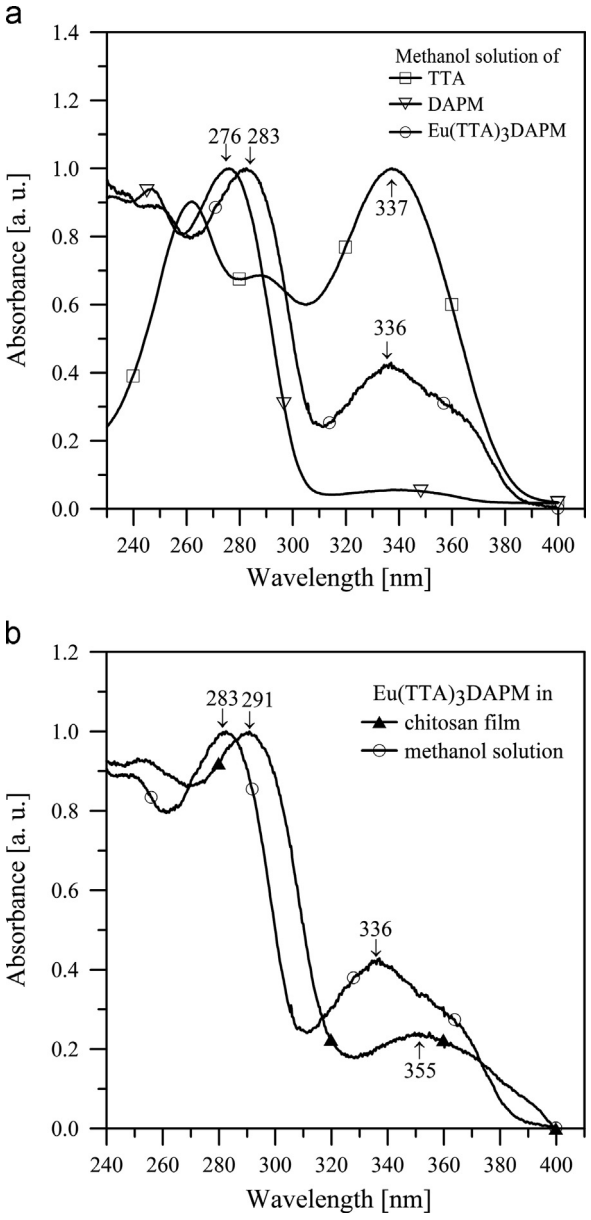

Fig. 2. Absorption spectra of (a) diantipyrylpropylmethane (DAPM), thenoyltrifluoroacetone (TTA) and $Eu(TTA_3)DAPM$ in methanol solution and (b) europium complex $Eu(TTA_3)DAPM$ in methanol solution and in chitosan film (5.45% $Eu(TTA_3)$ DAPM, film thickness 24 μm).

of Eu complex in solution and chitosan film are slightly shifted to larger wavelengths as compared with absorption peaks of TTA and DAPM in methanol solution. Chitosan film in the region 220–400 nm is transparent.

Photoluminescence (PL) spectrum of $Eu(TTA)_3DAPM$ (5.45%) doped chitosan film is shown in Fig. 3. Excitation at 350 nm produces five narrow emission peaks centered at 579 nm, 591 nm, 612 nm, 652 nm, and 708 nm which are related to $^5D_0 \rightarrow {}^7F_J$ transitions ($J=0$, 1, 2, 3, 4) of Eu^{3+} ion. The peaks may reveal fine structure, because ^7F_J ($J=1$, 2, 3, 4) levels are degenerate and split into $2J+1$ sublevels.

Luminescence due to non-degenerate $^5D_0 \rightarrow {}^7F_0$ transition appears as a single peak, which should be fitted by one gaussian (peak maximum 579.7 nm) in energy domain. The gaussian fit of this band is shown in the inset in Fig. 3. It indicates that in chitosan $Eu(TTA)_3DAPM$ film there is one dominant type of the complex.