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## Sensitized green emission of terbium with dibenzoylmethane and 1, 10 phenanthroline in polyvinyl alcohol and polyvinyl pyrrolidone blends



Brijesh Kumar, Gagandeep Kaur\*, S.B. Rai

Laser and Spectroscopy Laboratory, Department of Physics, Banaras Hindu University, Varanasi 221005, India

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### ABSTRACT

Tb doped polyvinyl alcohol: polyvinyl pyrrolidone blends with dibenzoylmethane (DBM) and 1, 10 Phenanthroline (Phen) have been prepared by solution cast technique. Bond formation amongst the ligands and  $Tb^{3+}$  ions in the doped polymer has been confirmed employing Fourier Transform Infrared (FTIR) techniques. Optical properties of the  $Tb^{3+}$  ions have been investigated using UV-Vis absorption, excitation and fluorescence studies excited by different radiations. Addition of dimethylbenzoate and 1, 10 Phenanthroline to the polymer blend increases the luminescence from  $Tb^{3+}$  ions along with energy transfer from the polymer blend itself. Luminescence decay curve analysis affirms the non-radiative energy transfer from DBM and Phen to  $Tb^{3+}$  ions, which is identified as the reason behind this enhancement. The fluorescence decay time of PVA-PVP host decreases from 6.02 ns to 2.31 ns showing an evidence of energy transfer from the host blend to the complexed Tb ions. Similarly the lifetime of DBM and Phen and both in the blend reduces in the complexed system showing the feasibility of energy transfer from these excited DBM and Phen to  $Tb^{3+}$  and is proposed as the cause of the above observations. These entire phenomena have been explained by the energy level diagram.

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### 1. Introduction

Polymer matrices are of budding significance for hosting the rare earth (RE) ions. Bearing in mind, the ample applicability of RE doped polymers, their compactness, competence and stumpy expense, these materials have been the focus of passionate research now-a-days [1]. RE doped polymers possess numerous advantages, viz. suppleness of shape, thickness, size, high electro-optic and thermo-optic coefficients [2,3]. The high luminescence efficiency from RE doped polymer combined with high color purity of emission may authorize these for next generation phosphor screens and display devices [4]. Highly luminescent rare-earth complexes with  $\beta$ -diketonates and carboxylic acids have been the subject of intensive studies owing to their potential applications as luminescent and laser materials, efficient organic light emitting diodes and polymer light emitting diodes [5–8].

The scientific and technological curiosity in polymer blends is noticeably full-fledged because polymer blending provides prospects to tailor the ultimate artifact with utmost requirements of the applications which cannot be achieved by one polymer alone [9–11]. However, the manifestation of superior properties depends upon the miscibility of blend [12]. Poly(vinyl alcohol) (PVA), Poly(methyl-methacrylate) (PMMA), Polyethylene (PE), Polystyrene (PS) and polycarbonates belong to the majority of trendy polymer matrices used as a host for luminescent RE complexes. Amid the polymers, PVA has exceptional physical properties such as mechanical strength, electrochemical stability, non-toxicity, good film-forming capability and biocompatibility. It contains hydroxyl group attached to methane carbons. These hydroxyl groups can be a source of hydrogen bonding [13]. Polyvinylpyrrolidone (PVP) is an amorphous non-ionic polymer soluble in water and organic solvents possessing fair film forming ability, surface activity, good adhesive properties, stability in acidic or basic media, good biocompatibility and low toxicity [14,15]. It possesses high glass transition temperature (T<sub>g</sub>) because of the presence of rigid pyrrolidone group which draws polar group rapidly and is known to form various complexes with

\* Corresponding author.

E-mail address: [gagandeep\\_bhu@yahoo.com](mailto:gagandeep_bhu@yahoo.com) (G. Kaur).

other polymers. Consequently, a hydrogen-bonding interaction may take place between these two polymers [16]. The blending of these polymers is stable within the physiological environment because of physical cross-links consisting of intermolecular hydrogen bonds and intramolecular hydrogen bonds within PVA, which is responsible for the solubility of PVA and PVP in water and their miscibility in all proportions [17]. Recently, Kumar et al. [18] have demonstrated enhanced photoluminescence of  $Mn^{2+}$  and  $Tb^{3+}$  ions doped PEO + PVP by an effective energy transfer of  $Tb^{3+}$  to  $Mn^{2+}$  ions in blended films. Abdelrazek et al. have studied structural, optical, thermal and morphological studies for pure PVA/PVP blend and PVA/PVP blend filled with different concentrations of chitosan and lithium bromide using casting method [12,19]. A biodegradable solid polymer blend electrolyte has been prepared by using polyvinyl alcohol (PVA) and polyvinyl pyrrolidone (PVP) polymers with different molecular weight percentages of ammonium acetate, and its structural, thermal, vibrational, and electrical properties were evaluated by Rajeshwari et al. [20]. PVP polymers containing Li + or Ag + ions have been synthesized in good stability and transparency by using the solution casting method by Sivaiah et al. [21] and shown the applicability in electrochemical display device applications. Karbowski et al. have studied the interaction of lanthanide  $\beta$ -diketonate complexes with polyvinylpyrrolidone (PVP) has been systematically investigated using fluorescence spectroscopy [22].

The intention of the present work is to explain the possibilities of fabrication of new polymer composites blending PVA and PVP polymers containing rare earth ions to make them useful in technological applications. In this work, we have prepared terbium (III) benzoate with 1, 10-Phenanthroline in PVA-PVP blends and carried out detailed investigations on their optical properties.

## 2. Experimental

Terbium oxide, Dibenzoylmethane (DBM) and 1, 10-Phenanthroline (Phen) used are 99.9% pure. These compounds alongwith polyvinyl alcohol (PVA, mw. 14,000 g mol<sup>-1</sup>) and poly-vinylpyrrolidone (PVP, mw.13,000,00 g mol<sup>-1</sup>) were purchased from Sigma Aldrich and used without further purification.

### 2.1. Synthesis Process of $Tb(DBM)_3Phen$ Complex

0.01 M solution of  $Tb^{3+}$  was prepared by dissolving a known amount of  $Tb_4O_7$  in hydrochloric acid. Separately, the complexes of organic-RE ion were prepared by mixing the ethanolic solution of DBM (2.3 wt%) and 1, 10-phenanthroline (Phen) (0.56 wt%) to the previously prepared solution (0.01 mol L<sup>-1</sup>) of terbium chloride in 3:1:1 ratio as described in our previous work [23]. Mixture thus prepared was evaporated to dryness in a petri dish at room temperature over a course of time in air to obtain transparent blend films of desired constituents.

### 2.2. Characterization

The absorption spectra of the samples were recorded using a Perkin Elmer Lambda 750 UV-Vis-NIR spectrophotometer. Fourier Transform Infra-Red (FTIR) spectra were recorded using Perkin Elmer FTIR/FIR spectrometer Frontier. Excitation and emission spectra were monitored using Fluorolog-3 spectrometer (model: FL3-11, Horiba JobinYvon Edison MJ USA). Nanosecond life time was measured using time resolved fluorescence spectrometer [Edinburgh Instrument Ltd.]. Excitation source used in lifetime measurement is a pulsed diode laser of wavelength 303 nm (pulse width 775.2 ps, bandwidth 9.6 nm). 25 W Xe pulsed lamp was used for  $\mu$ s lifetime measurements.

## 3. Results and Discussion

### 3.1. UV-Vis Absorption

UV-Vis absorption spectra of PVA, PVP and PVA-PVP blend were recorded in the range of 220–500 nm and are shown in Fig. 1(A). The absorption spectrum of PVA film contains a characteristic band at 270 nm assigned to  $\pi \rightarrow \pi^*$  electronic transition of PVA molecule. The UV-Vis spectrum of PVP exhibits a narrow band at 260 nm, which may be assigned to  $n \rightarrow \pi^*$  transitions between the oxygen lone pairs and the vacant  $\pi^*$ -orbital of the pyrrolidone ring. But the absorption itself for the blended film of PVA/PVP is not observed in the present case.

UV-Vis absorption spectra of  $Tb^{3+}$  ion,  $Tb^{3+}$  ion with Phen,  $Tb^{3+}$  ion with DBM and  $Tb^{3+}$  coordinated complex of DBM and Phen doped in PVA-PVP blend in the range of 220–500 nm under identical conditions and is shown in Fig. 1(B). No clear absorption band of  $Tb^{3+}$  is resolved in case of  $Tb^{3+}$  ion in PVA-PVP blend film. The absorption curve for  $Tb^{3+}$  ion doped with Phen shows very clearly a band at 266 nm with a weak shoulder at 290 nm which attributes for the electronic transitions of the aromatic ring of Phen. UV-Vis absorption spectrum of  $Tb^{3+}$  ion with DBM blend consists of band at 250 nm corresponding to  $S_2 \leftarrow S_0$  transitions of DBM and at 350 nm which arises due to  $n \rightarrow \pi^*$  transition of ligand. UV-Vis absorption spectrum of  $Tb(DBM)_3Phen$  complex doped PVA-PVP blend consist of bands at 266 and 290 nm due to  $n \rightarrow \pi^*$  transition of Phen along with 350 nm absorption of DBM respectively.

### 3.2. FTIR Analysis

Information pertaining to vibrational features and molecular structure of  $Tb(DBM)_3Phen$  complex in polymer blend of PVA-PVP can be obtained from FTIR studies. Any interaction amongst the constituents leads to up field or down field shift in wave numbers by the vibrational modes of the molecules in that particular system. Infrared absorption spectra of different constituents viz. PVA, PVP, PVA-PVP blend and

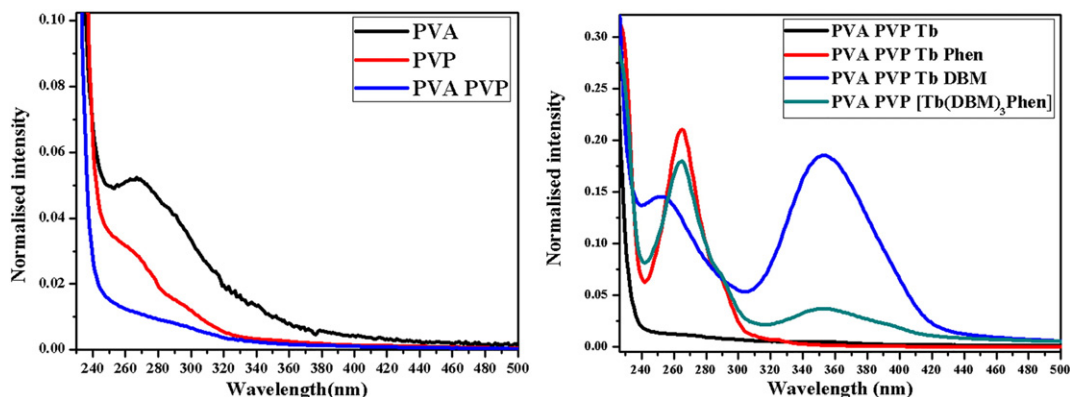


Fig. 1. (A) UV-Vis absorption spectra of PVA, PVP and PVA-PVP blend recorded in the range 220–500 nm. (B) UV-Vis absorption spectra of  $Tb^{3+}$  ion,  $Tb^{3+}$  ion with Phen,  $Tb^{3+}$  ion with DBM and  $Tb^{3+}$  coordinated complex of DBM and Phen doped in PVA-PVP blend in the range 220–500 nm.

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