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Concentration influence on the photoluminesces properties of terbium complexes with β -diketonate doped PMMA polymer

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Abstract : Terbium complexes doped PMMA polymer rod shape samples were synthesized at several concentrations. The vibronic transitions, absorption as well as emission for Tb³⁺ ions have been discussed in polymer host. The concentration quenching creates luminescence decay then reduction in the energy transfer to the Tb³⁺ ions from the surrounded ligand. Where the energy transfer processes in aggregates of Tb³⁺ doped PMMA can cause diminishing of some ⁵D₄ → ⁷F_J transitions. All utilized

doped samples show strong characteristic emission bands of terbium ion ⁵D₄ → ⁷F_J (J = 6, 5, 4 and 3) and the emission transition centred at 544 nm corresponds to ⁵D₄ → ⁷F₅ transition, characteristics of this lanthanide cation, is the dominant one.

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Keywords : Tb complexes; PMMA; Spectroscopy; Concentration; Energy transfer.

INTRODUCTION

In recent years, lanthanide ions containing photonic materials have attracted much attention for their potential applications for full color displays, optical sources and laser systems^[1-6].

Crystals doped with lanthanide ions are conventional materials for accomplishing lasing action. However, there has been considerable interest in the development of new photonic materials such as polymers^[7, 8].

As a polymer material, Polymethylmethacrylate (PMMA) attracted particular interest, for its low

simple synthesis, low cost and optical absorption in the visible region^[9]. The immobilization of the complexes in flexible, transparent matrices facilitates their application, especially for optical devices used in the visible and NIR area. Polymers doped with lanthanide complexes have been investigated for optical amplification^[10,11] and prototypes of flat panel displays containing lanthanide complexes have been presented^[12,13].

Every lanthanide complex requires the incorporation into the ligand structure of a sensitizing chromophore, capable of transferring its excited state energy to the encapsulated

lanthanide(III) ion. The emission spectra of lanthanide ions and their complexes consist of very narrow bands because they arise from inner-shell electronic transitions that are unaffected by the environment and occur at well-defined wavelengths^[14]. In lanthanide emitter, the concentration quenching that result from the use of closely spaced multiple fluorophores or lumiphores (compounds that luminesce) is minimized because the narrow emission band has minimal overlap with the excitation band^[15].

Tb(III) complex emission in the green wavelength range of visible light has been studied for detection of bacterial endospores in soil, determination of carbofuran in water, enhance formation of singlet oxygen, coupling of Fe₃O₄ nanoparticles for magnetic resonance imaging applications and ZrO₂-based fluorescent Tb(III) nanoparticles have been prepared as a fluorescent nano-probe for time-resolved fluorescence bioassay^[16-20].

Because of its huge optical applications, Tb ion doped polymer is of great interest to study its luminescent properties. In this work, Tb β -diketonate complexes was synthesized and incorporated into PMMA structure. As well as the spectroscopic of Tb⁺³ ions doped into polymer matrices were presented as a function of Tb⁺³ concentration, to probe the influence of this matrix on Tb excitation and emission spectra.

EXPERIMENTAL

Material

The following chemical materials were used in this work, Terbium chloride TbCl₃·6H₂O and ThenoylTrifluoroAceton (htta) C₈H₅F₃O₂S, both supply from Sigma-Aldrich Co, Methylmethacrylate MMA C₅H₈O₂ Molecular weight g/mol 100.12 and Benzoyl peroxide (Bp) C₁₄H₁₀O₄ both supplied from HIMEDIA, Ethanol (spectroscopy grade) supplied from Gainland Chemical Company and deionized water.

Samples synthesis

First, benzoyl peroxide BP was dissolved in MMA. Bubbled nitrogen gas through the monomer

for ~ 10min to deoxygenate the solution (oxygen is a radical scavenger). The solution placed in a water bath at 60°C with plastic floats. Dissolve fix amount of TbCl₃ in deionized water, this solution divided into two parts. The first part used for preparing five TbCl₃ solutions at ion concentrations (0.6, 1.2, 6, 12 and 60) × 10²⁰.

While the second part mixed with NaOH and htta quickly, then distilled water, white solution containing a stuck achieved. By heating this solution to 70 °C we get a white precipitate by slow evaporation.

The precipitate washed several times by distilled water and filtered by candidacy paper, then dried using vacuum oven at 75 °C for two hours yielding dry powder.

This powder was dissolved in deionized water for preparing five Tb- β dicetonate solutions at ion concentrations (0.6, 1.2, 6, 12 and 60) × 10²⁰. Both TbCl₃ and Tb- β dicetonate solution mixed with polymer by stirring at room temperature over a period of one day, then casting in a rod shape.

UV-Vis absorption spectra for both solutions and doped PMMA samples of terbium chloride and complex were recorded using a spectrophotometer model (1800UV), from Thermo Corporation (UK). Photoluminescence (PL) spectra of the above solution and final doped samples solutions were recorded using Elico Limited SL 174 Spectrofluorometer, India. The optical path length was 10 mm with pure solvent or polymer being used as a reference.

RESULT

Absorption spectra

First, for comparison purpose, the absorption spectrum of the prepared pure PMMA rod is illustrated in Figure (3-1). From this figure, it is clear that, the PMMA rod has almost transparent feature in the entire visible region (400-700 nm). As well as, the polymer has significant absorption band in the UV region (200-350 nm). The transparent percentage of this polymer was about 94%, which calculated from the transmission spectrum in the visible region.

Figure (2) illustrate the absorption spectra for

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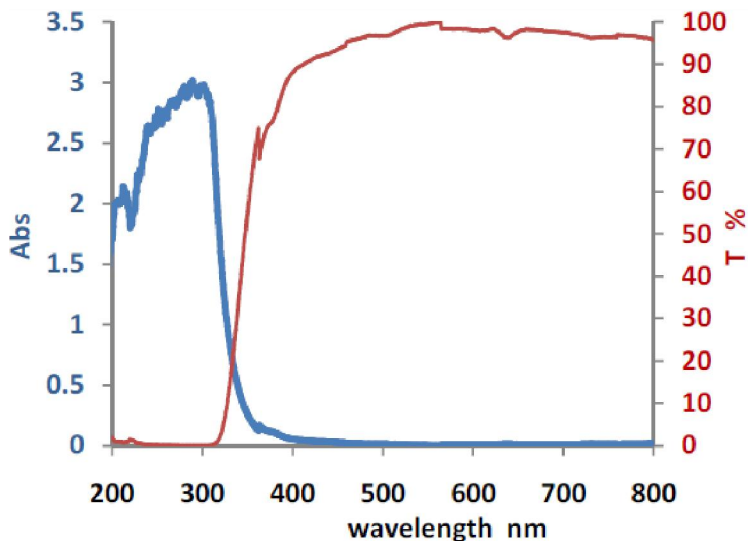


Figure 1 : Absorption and transmission spectrum of PMMA

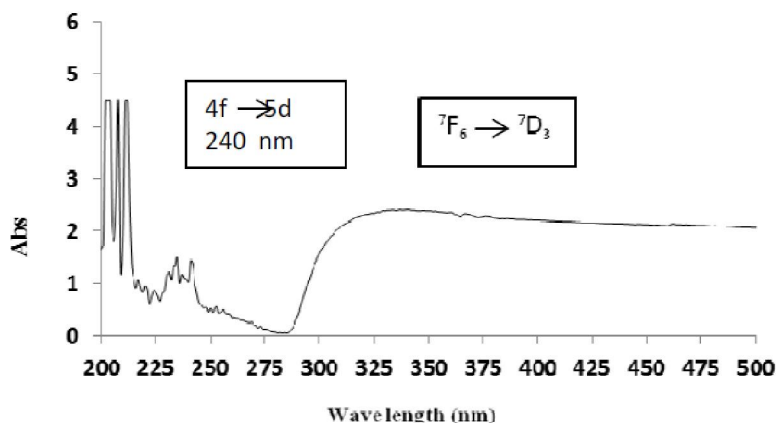


Figure 2 : Absorption spectrum for TbCl_3 dissolved in water at different concentration

terbium chloride in water solution at concentration of 10^{-2} M. It can be observed two absorption bands.

The first band extended below 280 nm, where the observed main excitation bands at about 240, 265 nm may be associated with the allowed low spin (LS) $5d_2$, $5d_1$ transitions^[21]. While the second band was broad and it extends above 280 nm. This band may be attributed to the overlapping between several sub bands. The first one is the absorption band at 320 nm, which due to forbidden high spin (HS) $5d_1$ f-d transitions.

The second sub band is the absorption to the higher energy levels of Tb^{+3} ions, 5L_8 , 5L_9 , $^5L_{10}$, 5G_6 ($4f^4f$) \rightarrow which lies between 280 - 378 nm^[21]. The third sub band is belong to the main transitions $^7F_J \rightarrow ^5D_3$ and $^7F_J \rightarrow ^5D_4$, which belong to the main Tb^{+3} ions transition.

The absorption spectra for terbium chloride

doped PMMA were presented in figure (3). From this figure, there are two main bands, well distinguished. The first one, which is corresponding to the transition from ground state to the higher state, f-d transition, located around 241 nm (5.16 eV), which was considered in this work as excitation wavelength, while the second band is the same as mentioned in solution case.

Emission spectra

The emission spectra of TbCl_3 doped PMMA, which dissolved in ethanol at different concentrations are shown in figure (3), it is obviously noticed from this figure that the intensity of the overall the intensity of the recorded $^5D_3 \rightarrow ^7F_6$ transition is about four times greater than that of $^5D_3 \rightarrow ^7F_4$, $^5D_3 \rightarrow ^7F_5$ and $^5D_4 \rightarrow ^7F_J$ transitions.

In the case of terbium complex, four emission

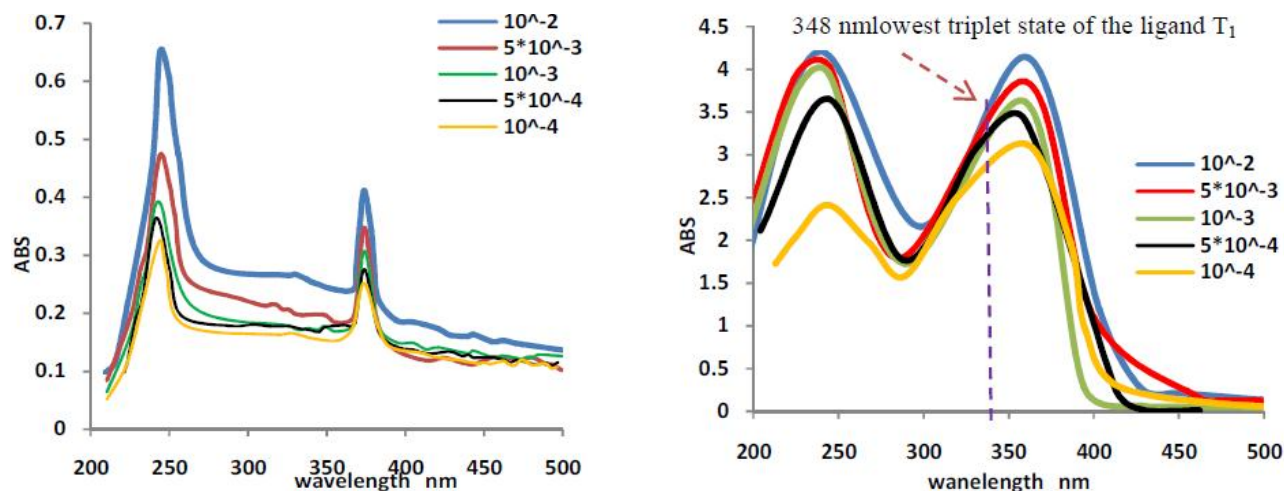


Figure 3 : Absorption spectra of PMMA doped in a) TbCl_3 b) Tb complex at various concentrations

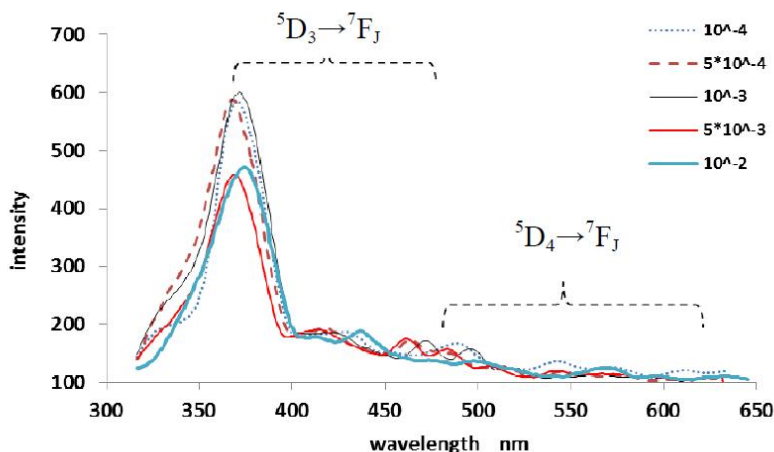


Figure 4 : Emission spectra of TbCl_3 doped PMMA at various concentrations

peaks are observed of the ${}^5\text{D}_3 \rightarrow {}^7\text{F}_6$ and ${}^5\text{D}_4 \rightarrow {}^7\text{F}_J$ ($J = 3 - 6$) transitions after excitation at 240 nm. The positions of the major peaks are the same, because of the good shielding of the $4f$ electrons from the environment. Minor differences can occur in the peak splitting and the intensity ratio between these peaks.

The first look on these spectra is demonstrating the comparable intensities of ${}^5\text{D}_4 \rightarrow {}^7\text{F}_6$ and ${}^5\text{D}_3 \rightarrow {}^7\text{F}_J$ see Figure (4).

Another indication from this sample is the intensities of these peaks are concentration systematically dependence. Where in the case of ${}^5\text{D}_4 \rightarrow {}^7\text{F}_J$ transitions the samples prepared at concentration of 5×10^{-3} [M] give higher emission intensities for all ${}^5\text{D}_3 \rightarrow {}^7\text{F}_J$ transitions as well as in ${}^5\text{D}_3 \rightarrow {}^7\text{F}_6$ transition. While in the case of the peaks lay at 444 nm and 427 nm, which belong to ${}^5\text{D}_3 \rightarrow {}^7\text{F}_5$ and ${}^5\text{D}_3 \rightarrow {}^7\text{F}_4$ transitions, the concentration which yield higher in-

tensities is 5×10^{-4} [M] see Figure (4-b).

DISSUASION

Regard to the absorption spectra for PMMA doped in TbCl_3 as well as Tb complex, for all doped concentrations the two main bands intensities are increase systematically as the doping concentrations increases, this increasing undergoes Beer lambert law. While the affection of the doping concentration on the absorption bands position is weak. However, at highest concentration, slight red shift occurs in the first band, whereas the second band kept fixed.

The intensities of the two absorption bands in the case of Tb complex doped PMMA samples are seven times greater than that in TbCl_3 doped PMMA samples. This may be due to the well-distributed Tb ion, within the complex, inside the polymer in compare to the case of Tb ions as TbCl_3 inside the poly-

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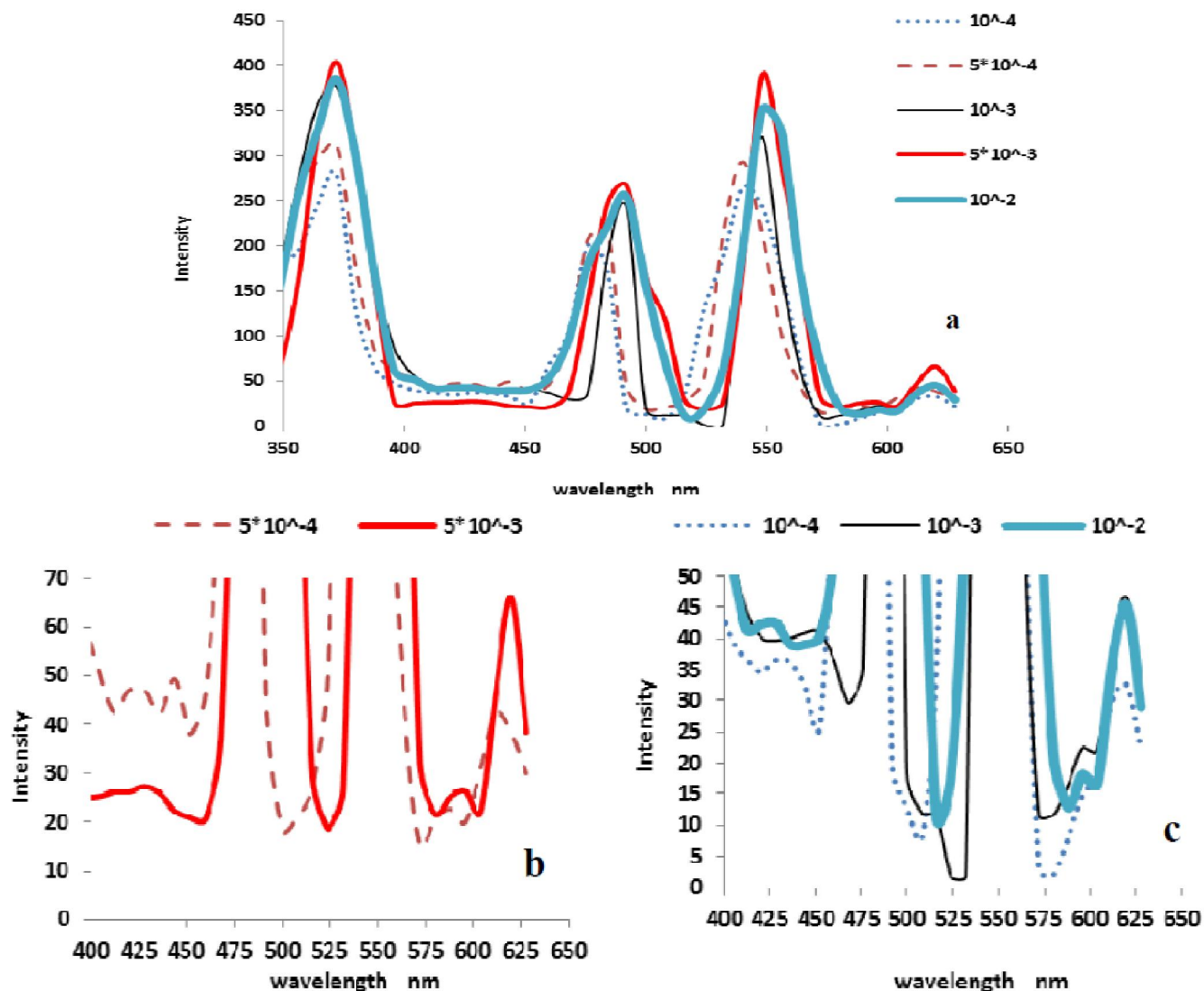


Figure 4(b) : Emission spectra of Tb complex doped PMMA at various concentrations a) large scale b) and c) small scale

mer.

It is clear that the solid host has dispersed the terbium complex molecules (caged them) then prevent aggregation, yielding enhancement of their absorption. While Tb^{3+} ions are themselves insoluble in polymers, encapsulation of the ions by complexation with organic ligands allows incorporation within polymer matrices^[22, 23].

In addition to their useful light harvesting properties, the organic ligands also protect lanthanide ions from the local environment by acting as a physical buffer. This shielding effect considerably reduces non-radiative de-activation processes arising from coupling with lattice, residual water (O–H bond) or solvent molecule vibrations^[24–26].

However, in Tb complexes, Tb^{3+} ion is completely coordinated by eight oxygen atoms in and hence does not need to cluster with another ion to complete its valence. Thus, polymer materials may be doped at relatively higher concentrations with complexes and may consequently exhibit high luminescence yields under UV excitation without quenching^[27].

Latva and co-workers observed that energy back-transfer from the excited terbium ion to the ligand occurs when the energy difference between the 5D_4 level of Tb^{3+} and the lowest triplet state of the ligand is lower than 1850 cm^{-1} ^[28]. In our study the energy difference between the triplet state of the coordinated Tb ligands and the 5D_4 level of Tb^{3+} is

around 2280 cm^{-1} (348–378 nm) see Figure (3-b), a value that allows a good energy transfer.

If the electrons on the ligand are excited, the possibility therefore exists that, instead of falling back to the ground state of the ligand, they might pass first to the excited state of the Tb^{3+} and then fall to the metal ground state, emitting radiation of characteristic frequency in doing so luminescence. In this process, light energy is absorbed by complex ligands leading to excitation of each ligand from the ground state (S_0) to the Franck–Condon excited state, followed by relaxation to the excited singlet state (S_1). Intersystem crossing then results in formation of the triplet excited state ($T_1 \approx 248\text{ nm}$ in our study Figure (3-b)) from which, if the energy of the triplet level is higher than that of the emission level of the Tb ion (374 nm), energy transfer may occur to the upper excited states of the Tb ion^[16,17]. A too small energy gap however will lead to back energy transfer from the lanthanide ion and possible bimolecular quenching of T_1 by dioxygen. However, due to the low oxidation potential of Tb^{3+} , the ion can be oxidized to Tb^{4+} , which does not show emission.

This is essential as direct excitation of the Tb^{3+} ion is very inefficient, leading to low values of ϵ ($\leq 1\text{ M}^{-1}\text{ cm}^{-1}$) as the relevant f–f transitions are parity (Laporte) forbidden^[29].

Four emission peaks are observed of the ${}^5\text{D}_4 \rightarrow {}^7\text{F}_j$ ($J = 3 - 6$) transitions after excitation at 240 nm. The positions of the major peaks are the same, because of the good shielding of the 4f electrons from the environment. Moderated differences can occur in the peak splitting and the intensity ratio between the peaks.

CONCLUSIONS

In conclusion, the results clearly illustrate that the utilizing terbium complex will optimize the luminescence condition. Where the initiated of ${}^5\text{D}_4 \rightarrow {}^7\text{F}_j$ transitions as well as ${}^5\text{D}_3 \rightarrow {}^7\text{F}_j$ transitions at comparable intensities will be achieved easily by using Tb^{3+} complex instead of terbium chloride dopant.

The effect of concentration quenching and luminescence decay has indicated that the energy trans-

fer type among Tb^{3+} ions in PMMA is one of important factor that diminish the luminescence properties.

The luminescence of the Tb^{3+} complex-doped PMMA figure is changesignificantly with the variation of complex doping concentration.

The energy transfer processes in aggregates of Tb^{3+} doped PMMA, which causes diminishing of some ${}^5\text{D}_4 \rightarrow {}^7\text{F}_j$ transitions, make the concentration quenching process come true, this can be overcomes by utilizing complexes.

Under the excitation wavelength of 240nm, all utilized doped samples show strong characteristic emission bands of terbium ion ${}^5\text{D}_4 \rightarrow {}^7\text{F}_j$ ($J = 6, 5, 4$ and 3) and the emission transition centred at 544 nm corresponds to ${}^5\text{D}_4 \rightarrow {}^7\text{F}_5$ transition characteristics of this lanthanide cation is dominant one.

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ORIGINAL ARTICLE

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