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Intensification of luminescence of Europium-EDTA complex in polyvinyl pyrrolidone films by copper nanoparticles☆

Renata Reisfeld [a, b, *], Viktoria Levchenko [a, b], Agata Lazarowska [c], Sebastian Mahlik [c], Marek Grinberg [c]

[a] Institute of Chemistry, The Hebrew University of Jerusalem, E. Safra Campus, Givat Ram, 91904 Jerusalem, Israel
[b] The Harvey M. Krueger Family Center for Nanoscience and Nanotechnology, The Hebrew University of Jerusalem, Edmond J. Safra Campus, 91904 Jerusalem, Israel
[c] Institute of Experimental Physics, Gdańsk University, Wita Stwosza 57, 80-952 Gdańsk, Poland

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ABSTRACT

Stable copper nanoparticles (CuNPs) were prepared and incorporated into polyvinylpyrrolidone (PVP) films together with pre-prepared complex of europium-ethylenediaminetetraacetic acid (EuEDTA). From the comparison of the excitation spectrum of the complex alone and of the complex in conjunction with CuNPs an increased fluorescence intensity of the complex is observed as the result of interaction of the complex with surface plasmons of copper. This effect is maximal when the extinction band of CuNPs coincides with the absorption maximum of the complex, as much more light reaches the excited state of europium in the complex during the excitation events as the result of light scattered by copper plasmons. An additional band was observed in the excitation spectrum of the complex in co-doped by the CuNPs around 320÷390 nm which we attribute to electron transfer from CuNPs to excited state of europium.

1. Introduction

The lanthanides are a fascinating group of elements the optical properties of which arise from the inner f-electrons which are starting with one in Cerium and terminate with thirteen in Ytterbium. The transition probabilities within the 4 f-orbital are forbidden by Laporte rule and become partially allowed either by mixing with 5 d-orbital of Ln ion or with a charge transfer states of the neighboring ligands [1,2]. The basic theory of the electronic spectra can be found in Refs. [3–5].

Lanthanide luminescence is currently applied in the following fields. Luminescent solar concentrators [6,7], computer displays; light emitting diodes [8], semiconductor quantum dots [9], luminescent biosensors [10], bioassays [11], active optical waveguides [12], materials based on upconversion from IR to visible light [13], materials for optoelectronics [14]. The importance of lanthanides in solar energy conversion can be found in excellent book [15].

The luminescent spectra of the europium are intensified greatly by complexation of lanthanide ions with organic ligands. These lanthanide ions form stable crystalline complexes with heterocyclic ligands, such as bipyridyl (bpy) and phenanthroline (phen), which exhibit efficient energy transfer to the chelated lanthanide ions [16,17] and cryptates [18].

However, lanthanides complexes with organic ligands for practical uses are limited because of poor thermal stability and mechanical properties, although they also have good phosphor characteristics. This drawback can be overcome by protecting them by a glassy or stable polymer surrounding [19].

Recently nanoparticles (NPs) of lanthanides having high luminescence have shown numerous applications in medicine and other fields. In order to take the advantage of the properties of the lanthanides additional ways of increasing their fluorescence intensities are studied. This is done by incorporating into the host matrices NPs of silver, gold and copper [20–22] in conjunction with the luminescent species.

In the present paper we describe the intensification of EuEDTA

☆ Enrique Berman Professor of Solar Energy.

* Corresponding author. Institute of Chemistry, The Hebrew University of Jerusalem, E. Safra Campus, Givat Ram, 91904 Jerusalem, Israel.
E-mail address: renata.reisfeld@mail.huji.ac.il (R. Reisfeld).

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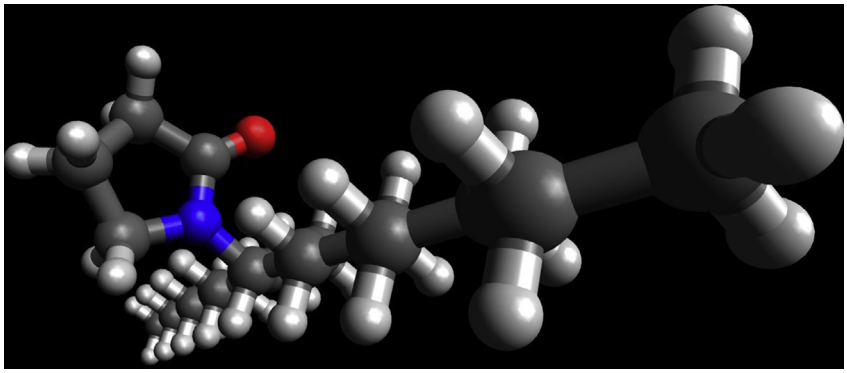

Fig. 1. The 3D-structure of PVP, red atom is oxygen, blue – nitrogen, dark grey – carbon, light grey – hydrogen.

complex incorporated in PVP and study the steady state and dynamic spectroscopy. The size and distribution of the CuNPs are obtained by scanning electron microscope (SEM) and transmission electron microscope (TEM).

2. Experimental

2.1. Preparation of EuEDTA complex in PVP

The EuEDTA complex in PVP matrix, see the structure of PVP in the Fig. 1, was formed as follows: appropriate stock solutions of desired metal ion europium chloride and ligands - ethylenediamine tetraacetic acid (see the structure of EDTA in Fig. 2) in 1:1 ratio were mixed in solution of sodium hydroxide/water/ethanol. Then 5 ml of this solution were incorporated in 5 ml of 15% PVP solution in ethanol followed by stirring for 3 h at 70 °C. Fig. 3 demonstrates the chemical structure of EuEDTA chelated complex.

Concentration of Eu^{+3} ions in PVP solution was 0.013 mM/mL.

2.2. Preparation of nanoparticles of copper

The synthesis of CuNPs is based on a previous paper [22] modified as follows. The starting materials consist of $Cu(NO_3)_2 \cdot 5H_2O$ – 0.3 M, sodium citrate - 0.3 M, 100 ml of distillated water, surfactant $(C_{16}H_{33})N(CH_3)_3Br$ (CTAB) - 0.05 M, aqueous NaOH –drop by drop up to pH 7, 0.01 ml of polyethylene glycol and 0.03 ml of glycerin. The solution is stirred with magnetic stirrer at temperature 80 °C. During the process, the blue solution turns reddish the extinction spectrum of which (vide infra) is the evidence of presence of CuNPs. The extinction spectrum of the CuNPs in solution is presented in Fig. 4.

2.3. Preparation of the samples

Films were formed on microscope slides using drop-casting process, dried at 28 °C for 24 h and heated at 100 °C for 1 h.

Two types of films were obtained by drop casting method:

1) EuEDTA – PVP film doped by EuEDTA complex
2) EuEDTACuNPs – PVP film doped by EuEDTA complex and nanoparticles of copper

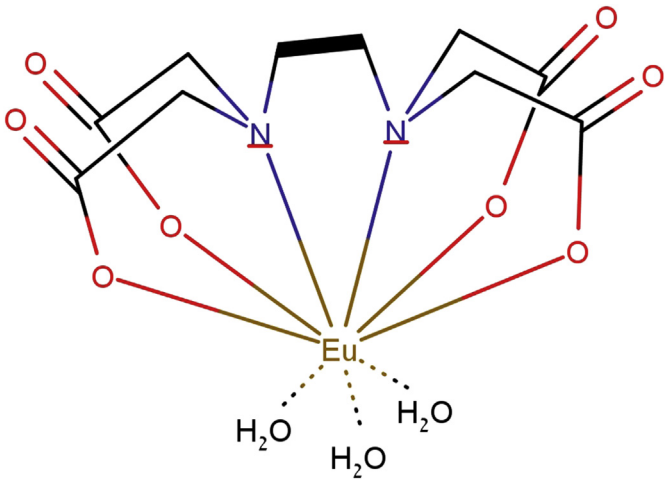

Fig. 3. The chemical structure of EuEDTA chelated complex.

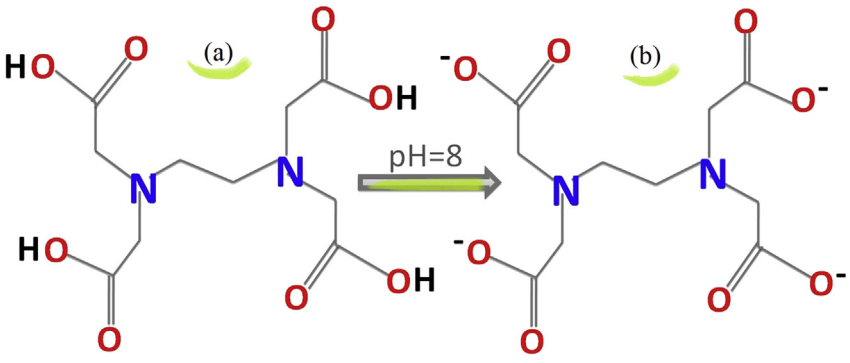

Fig. 2. The chemical structures of EDTA at classic (a), high pH alkaline (b) conditions.