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Determination of organophosphorus pesticides in water samples by using a new sensitive luminescent probe of Eu (III) complex



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ABSTRACT

This work describes the application of fluorescence for investigating the interactions of Eu(III)-TAN-1,10 phenanthroline (where TAN=4,4,4-Trifluoro-1-(2-naphthyl)-1,3-butanedione) with pesticides Chlorpyrifos, Malathion, Endosulfan, Heptachlor. The complex was synthesized and characterized by elemental analysis, FTIR, x-ray spectroscopy, solid fluorescence and thermal analysis. The results indicated that the composition of this complex is $[\text{Eu}(\text{TAN})_2(\text{Phen})(\text{H}_2\text{O})_2]\text{Cl}$. The luminescence properties of the complex in different solvents and at different pH values have been investigated. The results show that the complex exhibits more efficient luminescence at pH=7.5. The interactions of Eu-complex with different pesticides (Chlorpyrifos, Malathion, Endosulfan, and Heptachlor) in aqueous medium have been investigated by fluorescence measurements. The luminescence intensity of the probe is quenched by Malathion and enhanced by (Endosulfan, Heptachlor, and Chlorpyrifos). Direct methods for the determination of the pesticides under investigation have been developed using the luminescence variations of the probe in solution. The detection limits are 0.47, 1.02, 0.66, 0.64 $\mu\text{mol/L}$ for Chlorpyrifos, Endosulfan, Heptachlor, and Malathion, respectively. The binding constants and thermodynamic parameters of the pesticides with probe were evaluated. The emission quantum yield ($QY=0.71$) of Eu(III)-complex was determined using tris (2,2'-bipyridyl) dichlororuthenium(II) hexahydrate. A thermodynamic analysis showed that the reaction is spontaneous with negative ΔG . Effect of some relevant interferents on the detection of pesticides has been investigated. The new method was applied to the determination of the pesticides in different types of water samples (tap, river, and waste water).

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1. Introduction

Human poisonings and their related illnesses are clearly the highest price paid for pesticide use [1]. Over the last fifty years many human illnesses and deaths have occurred as a result of exposure to pesticides, with up to 20,000 deaths reported annually [2]. According to The Stockholm Convention on Persistent Organic Pollutants, 10 of the 12 most dangerous and persistent chemicals are pesticides [3]. Due to these results there is increasing anxiety about the importance of small residues of pesticides, often suspected of being carcinogens or disrupting endocrine activities.

The need for monitoring these residues in food, water and various environmental samples is the primary interest for many organizations to protect the human life. The United States Environmental Protection Agency (U.S. EPA) has imposed strict regulations on the concentrations of many environmental contaminants in air and water. According to the German drinking water regulation, the

concentration of individual pesticides in drinking water may not exceed the limit value of 100 ng/L [4]. So many researches have been developed in the last few years in this area to give a simple and direct method for the determination of the pesticides. These include chromatographic methods [5–11], electro and electroluminescence methods [12–14], UV-spectrophotometry, fluorescence, luminescence, and chemi-luminescence methods [15–18].

Among the various detection techniques, fluorescent probes make the best choice, since they are qualified with high sensitivity, high selectivity, fast response, and with direct detection [19].

Lehn [20] confirmed that lanthanide complexes with organic molecular structure have interesting photophysical properties which qualified them to be used as light conversion molecular devices (LCMDs). The design of efficient lanthanide complexes has become an important research goal, being pursued by several groups [21–26] and many luminescent lanthanide chelates are valuable alternative probes to conventional fluorophores [27].

The europium complexes have attracted more attention, due to their saturated red emission resulting from emitting strong fluorescence arising from f–f hypersensitive transition with a large Stokes shift (approx. 250 nm) and long lifetime (approx. several hundred μs)

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[28]. These distinct properties enabled the development of highly sensitive fluorescence chemical sensor. The intra-configuration $4f-4f$ transitions in rare earth ions are parity forbidden (Laporte rule), consequently the absorption and emission spectra of the RE(III) ions show weak intensity. However, the population of the excited states of the RE(III) ions may increase by coordination to organic ligands, which act as sensitizers. The ligands that present this property were called by Lehn as “antennas” [29]. In RE(III)-complex, the organic ligand absorbs and transfers energy efficiently to the metal ion (intra-molecular energy transfer) and consequently increases its luminescence intensity.

The β -diketone ligands are considered as most important organic ligands which have the ability to sensitize the luminescence of the Ln(III) ions, due to their strong absorption within a broad wavelength range originating from the $\pi \rightarrow \pi^*$ transitions.

Ternary rare-earth β -diketonates contain one or two additional ligands besides the β -diketonate ligands. These ligands act as Lewis bases, and form adducts with tris β -diketonate complexes because of the tendency of the rare-earth ion to expand its coordination sphere and to achieve a coordination number higher than six (typically eight or nine). Because the trivalent rare-earth ions are hard Lewis acids, the tris β -diketonate complexes form preferentially complexes with oxygen-donor or nitrogen-donor Lewis bases. 1,10 phenanthroline is the best choice for acting as second ligand due to its ability to enhance fluorescence intensity of the various binary complexes through synergistic effect, also its ability to fulfill the coordination numbers of the rare earth complexes [31–34]. Many sensitive and selective detection methods for the determination of pesticides in water include gas chromatography–mass spectrometry (GC–MS) and high performance liquid chromatography with either mass spectrometric (LCMS) or diode array detection (LC-DAD) [34]. These methods offer good limits of detection and wide linear ranges, but require high cost analytical instruments developed for the use in the laboratories. The necessary collection transportation and pretreatment of a sample is time consuming and a potential source of error. Significant progress has been achieved toward the development of luminescent chemosensors for different types of toxic pesticides. These chemosensors have several advantages over other methods.

However, chemical sensors are smaller, portable, less expensive devices and enable on-line and field monitoring and therefore can be a useful alternative tool [35].

This work describes the application of fluorescence methods for sensing pesticides Chlorpyrifos, Malathion, Endosulfan, and Heptachlor. It also includes the development of luminescence methods for detection of the investigated pesticides. The present paper is a part of our ongoing research for the development of chemosensors for determination of different types of pesticides based on molecularly imprinted polymers containing luminescent Eu(III) complexes. Such sensors will play an important role in minimization or elimination of false-positives. Due to the structural similarity of pesticide compounds, it is also paramount that the designed sensors must be fabricated such that they are highly selective toward specific pesticide compounds. This work represents a continuation of our work in the field of development of novel luminescent sensors for environmental and biomedical applications [35–38].

2. Experimental

2.1. Materials and solutions

All materials used in the present investigation were of AR Grade. Europium chloride hexahydrate ($\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$),

4,4-Trifluoro-1-(2-naphthyl)-1,3-butanedione (TAN) and 1,10 phenanthroline(Phen) were purchased from Sigma-Aldrich. All solvents used are in analytical grade quality include (methanol, ethanol, acetone, cyclohexane, ethylacetate, dimethylformamide, dimethylsulfoxide, and tetrahydrofuran) from Sigma-Aldrich.

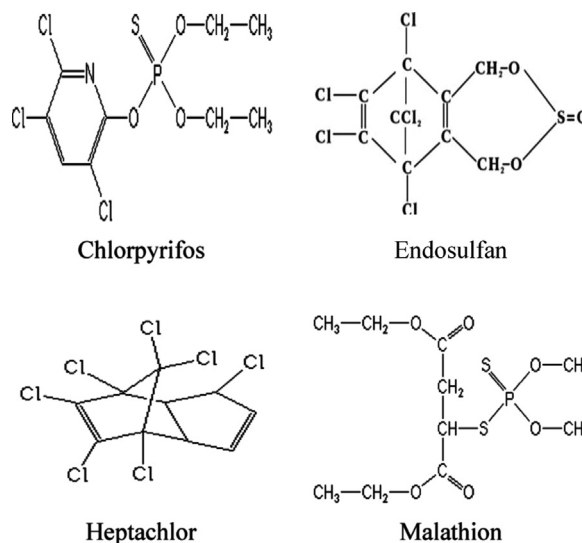
Pesticides used include (Chlorpyrifos, Malathion, Endosulfan, Heptachlor) were from Sigma-Aldrich. The structures of the studied pesticides are given in Scheme 1. Buffers used in this study include PIPES buffer (piperazine-N,N'-bis(2-ethanesulfonic acid)) ($\text{pH}=7.5$, $M=0.003 \text{ mol L}^{-1}$), TAPS buffer, TRIS buffer from Sigma-Aldrich. All salts used in this study include ammonium chloride (NH_4Cl), cobalt nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), sodium phosphate dibasic (Na_2HPO_4), potassium nitrate (KNO_3), calcium chloride ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$), sodium chloride (NaCl), cadmium nitrate ($\text{Cd}(\text{NO}_3)_2$), lead nitrate ($\text{Pb}(\text{NO}_3)_2$), copper nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$), nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), sodium carbonate (Na_2CO_3), potassium chloride (KCl) were from Sigma-Aldrich. Stock solutions were prepared using distilled, CO_2 free water.

2.2. Instrumentation

Luminescence spectra were acquired on a Jasco FP-6300 spectrofluorometer with a 150 W xenon lamp for excitation. Luminescence was excited at 365 nm and emission was collected at 614 nm. UV-absorption spectra were recorded with A Shimadzu-UV Probe Version 2.33 UV-visible automatic recording spectrophotometer with 1 cm quartz cell. Melting points were determined on a MEL-TEMP II apparatus (thermometer uncorrected); elemental analysis was carried out by Heraeus CHN-rapid analyzer; thermogravimetric analysis was carried out by SHIMADZU thermal analyzer Koyoto Japan. The infrared spectra were obtained in 4100 JASCO Japan FT-IR, x-ray spectra were recorded on a D8 advance Bruker, Germany (Cu target, $\lambda=1.54 \text{ \AA}$, 40 kV, 40 mA). Potentiometric pH measurements were performed on the solutions in a double-walled glass vessel at ($25 \pm 0.1 \text{ }^\circ\text{C}$) with a commercial Fisher combined electrode, and a magnetic stirrer was used. A fisher Accumet pH/ion meter Model 325 MP was used. The temperature was controlled using a thermostat controlling temperature within $\pm 0.1 \text{ }^\circ\text{C}$.

2.2.1. Determination of emission quantum yield

The emission quantum yield of $\text{Eu}(\text{TAN})_2(\text{Phen})$ complex was determined in toluene at concentration of $2 \mu\text{M}$ using tris (2,2'-bipyridyl) dichlororuthenium(II) hexahydrate in water ($\text{QY}=0.13$)



Scheme1. The structures of the studied pesticides

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