



ENERGY TRANSFER AND PHOTOCHEMICAL PROCESSES IN SYSTEMS OF INDUSTRIAL AND ENVIRONMENTAL IMPACTS

Thesis Submitted
By

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Summary

The area of energy transfer involving lanthanide ions has intrigued chemists, physicists, materials scientists, and biochemists due to the large number of applications in their respective disciplines. Lanthanide ions have been used to “probe” many structural and analytical problems such as the determination of local symmetries in crystalline inorganic materials, catalysis, probing the structure of biological macromolecules, and immunoassay using time-resolved luminescence. The search for new solid-state materials containing lanthanide ions is the goal of much advancement in the laser and telecommunication technologies.

The three most useful lanthanides, terbium or europium or samarium, have unusual spectroscopic characteristics, including millisecond lifetime, sharply spiked emission spectra, and large stokes shifts.

On the other hand, heterogeneous photocatalysis is often proposed for the elimination of organic pollutants from waste waters. The efficiency of TiO₂ photocatalyst, used as aqueous suspension, is experimentally proved for decomposition of most organic substances in water. TiO₂ has several advantages, especially low price and absence of toxicity. However, it involves a difficult problem of filtration to eliminate and recycle the catalysts after use.

Thus the objectives of this study focus on two points:

The first includes studying the factors affecting the light absorption and emission characteristics of some Tb³⁺, Eu³⁺ and Sm³⁺ complexes with five ligands (CAB, GA, 2-Pyr., DPPD, PDCA).

The second one is to remove remazol red RB 133 (RR RB 133), reactive blue 2 (RB 2) [as an examples of azodyes] and gallic acid [as an example of biocalcitrant] that have dangerous effects and a relatively high degree of solubility in water (i.e. they present in considerable amounts in waste water samples). Degradation processes implies the usage of UV-Visible photolysis in presence of immobilized TiO₂ photocatalyst.

This thesis consists of three chapters:

Chapter 1 deals with a general introduction of the subject. In **chapter 2**, the experimental procedures and instrumentations used are presented.

We have used the following spectroscopic methods for following up the energy transfer processes and light-induced interactions:-

- UV-Visible absorption spectroscopy.
- Fluorescence spectroscopy.
- IR spectroscopy

Moreover, TOC and COD analysis were performed to confirm the suggested degradation mechanism. Methods used for data treatments and handling such as chemical kinetics, quantum yield and determination of the apparent formation constant are included.

In **chapter 3**, we reported the results obtained in two parts as follows:-

Part I. Energy transfer processes

a- Spectroscopic characteristics.

We start studying some spectroscopic properties (Absorption and Fluorescence spectra) of the compounds under investigation in different media. Also the influences of different concentrations of ligands on the absorption and fluorescence spectra of Ln³⁺ ion will be spectrally studied and vice versa, in order to choose the best experimental conditions.

The absorption spectra of ligands are characterized by intense broad bands in the UV-region corresponding to the $\pi \rightarrow \pi^*$ transition. Upon complexation with Ln^{3+} (Tb^{3+} , Eu^{3+} and Sm^{3+}) ions, this bands is either red or blue shifted where the molar absorption coefficient is higher than the value corresponding to the free ligands.

Measurements of the emission spectra of complexes indicates the main luminescence line located at 545 nm assigned to the ${}^5\text{D}_4 \rightarrow {}^7\text{F}_5$ transition of Tb^{3+} ion, the main luminescence line located at 616 nm assigned to the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition of Eu^{3+} ion, and the main luminescence line located at 648 nm assigned to the ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{9/2}$ transition of Sm^{3+} ion. As the concentration of ligands increases we observed a marked increase in the emission intensities till reach the optimum concentration. Since less ligands in the inner coordination sphere of terbium ion must result in a lower degree of emission sensitization. Most of the spectra measured show that tris-terdentate chelation would be favored, except Tb-GA complexation that exhibits 1:5 molar ratio.

The strength of the formed complexes is determined by applying Benesi-Hildebrand equation. The results show that the complexation between Tb^{3+} ions and GA of $K_{\text{app}} = 181 \times 10^4 \text{ mol}^{-1} \cdot \text{L}$ is the strongest one compared to the other complexes [K_{appa} of (Tb-CAB) = $30.71 \times 10^3 \text{ mol}^{-1} \cdot \text{L}$, (Tb-2-pyr.) = $2.24 \times 10^3 \text{ mol}^{-1} \cdot \text{L}$, (Tb-PDCA) = $34.19 \times 10^3 \text{ mol}^{-1} \cdot \text{L}$, (Eu-PDCA) = $5.04 \times 10^3 \text{ mol}^{-1} \cdot \text{L}$, (Eu-DPPD) = $130.69 \times 10^3 \text{ mol}^{-1} \cdot \text{L}$ and (Sm-DPPD) = 58.04×10^3].

The absorption and fluorescence spectral data in different organic solvents indicate that complexation induces minor shifts in the energy of transitions, but the absorption and emission intensities differ from solvent to another. The observed decrease in quantum yield values in some aprotic and nonpolar solvents could be due to presence of two distinct

conformations of complexes occur in solution: one in which energy transfer to the lanthanide ion does not occur and one in which energy transfer is fast. For the Tb-CAB, Eu-DPPD and Sm-DPPD complexes, the luminescence intensities in DMSO and/or DMF solutions are stronger than in hydroxy solvent. This is attributed to vibrational energy transfer to the solvent molecules. It is well known that the excited state of the lanthanide ions is efficiently quenched by interactions with high-energy vibrations like O-H groups thereby the luminescence of these complexes in -OH containing solvents can be quenched easily because of the O-H oscillators.

The emission intensity and luminescence quantum yield of Tb-GA complex (in methanol), Tb-2-Pyr. (in ethanol), Tb-PDCA (in 1-propanol) and Eu-PDCA (in 1-butanol) is relatively higher than the other solvents, This indicates that Tb-GA, Tb-2-Pyr., Tb-PDCA and Eu-PDCA complexation is not susceptible to coordination of solvent molecules, which are known to act as effective quenchers of lanthanide luminescence via energy transfer into O-H, N-H, or C-H stretching vibrations. The observed decrease in quantum yield values in some aprotic and nonpolar solvents could be due to presence of two distinct conformations of complexes occur in solution: one in which energy transfer to the lanthanide ion does not occur and one in which energy transfer is fast. The results show no luminescence efficiency of Tb³⁺, Eu³⁺, Sm³⁺ in 1,4-dioxane indicating that the excited ligand is quenched by the vibrations of C-H of 1,4-dioxane.

b- Effect of incorporation in rigid matrices (PMMA and Sol-gel)

The effect of PMMA as a rigid medium on the luminescence intensity and quantum yield of Tb(III), Eu(III) and Sm(III) ions in their complexes is investigated. The results showed that there is no possibility for energy

transfer in Tb-CAB, Eu-DPPD and Sm-DPPD complexes in PMMA matrix. This could be attributed to a difficulty in Ln-complex inclusion in the cage of PMMA matrix as a result of unsuitable pore size. Also, the bulk size chlorine atom of CAB in Tb-CAB complex may cause a steric hindrance with the PMMA molecules which in turn prevent energy transfer. Also, the rigidity of PMMA matrix have been frozen the rotational motion established by DPPD during its complexation with Eu(III) or Sm(III) ions, therefore prohibit complexation. Unlike complexes of Tb-CAB, Eu-DPPD and Sm-DPPD, the complexes of Tb-2Pyr., Tb-GA, Tb-PDCA and Eu-PDCA exhibit energy transfer phenomena but the quantum yield values of Tb(III) and Eu(III) ions are found to be markedly lower compared to that in organic solvents and in sol-gel matrix. This could be attributed to less efficient antenna effect where under the excited state, the vibrations of ligands and polymer network would redirect some energy to non-radiation transitions, which would decrease the fluorescence lifetime and quantum yield.

Unlike PMMA and organic solution, sol-gel matrix is found to be a suitable host matrix for the luminescence of the studied complexes where the calculated luminescence quantum yield values in sol-gel matrix is higher than those in organic solvents and in PMMA matrix. This could be attributed to the relatively rigid host structure of sol-gel that limit the vibrations of the coordinated ligands with Tb(III), Eu(III) and Sm(III), resulting in decrease of the non radiative transition caused by vibrations and an increase in the luminescence quantum yield of Tb(III), Eu(III) and Sm(III) ions. This can be confirmed by the IR spectra of pure sol-gel, sol-gel containing rare earth complexes and correspondingly pure rare earth complexes. From the data, the excellent luminescence properties of rare earth complexes incorporated in silica matrix by sol-gel method can

make them promising candidates for potential use as luminescent material.

c- IR Spectroscopy

Measuring the IR spectra of the free ligands and their silica and non-silica complexes indicate either a red or blue shift in the characteristic absorption bands. Moreover, the appearance and disappearance of absorption bands is observed which in turn confirm complexation.

d- Effect of temperature on the luminescence Intensity of the lanthanide complexes in silica composites

The results indicate that the optimum temperature corresponds to maximum fluorescence intensity is $\approx 373\text{K}$, a temperature at which all water molecules are removed. On contrast, increasing temperature to 473K , results in decreasing the emission intensity. This could be attributed to the decomposition of the complexes indicating that the contribution from an energy transfer between the ligand and the Ln^{3+} ions becomes less efficient.

e- Excitation/Emission Matrix and Mapping of Luminescence:

This method seems to be useful as a qualitative identification tool. In particular, the location and relative intensity of peaks are suitable parameters for pattern recognition analysis as well as a useful new method in clinical chemistry and biochemistry.

Part II. Photocatalytic degradation using immobilized TiO_2 films

a- Absorption spectra

The absorption spectra of RR RB 133, RB 2 and GA were recorded in aqueous medium at room temperature where a relatively characteristic absorption peaks are obtained at 527, 614 and 265nm, respectively.

b- Photostability of RR RB 133 and RB 2 and GA

It was found that RR RB 133, RB 2 and GA have a high degree of photostability and direct photolysis in aqueous phase has not been found effective in their degradation. Also, both RR RB 133 and RB 2 are found to be photostable over the surface of LDPE-g-(4-vp/AAm) copolymer (without supported TiO₂).

c- Light-Induced interactions in presence of TiO₂ supported membranes

Upon irradiation of solid samples of RR RB 133 and RB 2 impregnated on the surface of TiO₂ supported LDPE-g-(4-vp/AAm) copolymer of different composites, a photo-assisted degradation reaction occurs. It was found that the photobleaching reactions obey first order kinetics and the photobleaching rate of impregnated RR RB 133 is markedly higher than the corresponding RB 2. This could be explained on the basis of adsorption competition of both RR RB 133 and RB 2 towards TiO₂ and/or copolymer sites. Also the presence of acrylamide and vinylpyridine-binder is suggested to be at the origin of the decrease in efficiency. We have also found that the color bleaching kinetics using copolymer 3 (of least TiO₂ content) is noticeably higher than the other types. This phenomenon is closely correlated to the electronic and textural copolymer properties and also may be due to the aggregation of TiO₂ particles at high concentrations, causing a decrease in the number of surface active sites. Also, this could be attributed to the light scattering and consequent reduction in light penetration through the copolymer films. Moreover, the synergetic effect of supported Ce³⁺ combined with immobilized TiO₂ decline the color bleaching rate compared to the pure TiO₂ supported copolymers. This could be attributed to increased concentration of holes in the valence band. Also, the Fermi level is shifted to lower values. This shift affects the position of the flat-band

potential of TiO_2 , which is shifted anodically, towards positive values with respect to the NHE potential.

Furthermore, heating the TiO_2 supported LDPE-g-(4-vp/AAm) copolymers and examining the photobleaching process results in a noticeable decrease in the photobleaching rate to half its initial value (without heating) due to decreasing the activity of titanium dioxide as a result of anatase – rutile transformation.

On the other hand, solar illumination of water sample contains GA in presence of TiO_2 supported on non-woven paper, results in a remarkable decrease in the UV-Vis. absorption spectrum of GA. It was noticed that the pH increases during the first 45 min of irradiation to reach and remains constant till the end of the experiment. This could be attributed to the destruction of carboxyl groups as CO_2 .

Moreover, the synergetic effect of Ru(II)-complexes combined with TiO_2 on the photomineralization kinetics of GA under the same experimental conditions is examined and is found to increase the photomineralization rate. This could be attributed to an effective electron scavenging of Ru-complexes to trap the CB electrons of TiO_2 which in turn sensitize the photocatalytic action of TiO_2 via transferring such trapped electrons to the surrounding adsorbed O_2 by oxidation process.

d- Total organic carbon (TOC) and chemical oxygen demand (COD) analysis.

It was found that when measuring the amount of total organic carbon (TOC) and chemical oxygen demand (COD) for aqueous solution of GA in presence of TiO_2 supported on non-woven paper before and after different intervals of solar illumination, a decrease in TOC and COD percentage of GA as a function of illumination time be 34.3% and 51.9% respectively. Moreover, the TOC and COD analysis show clearly that the

synergetic effect of TiO_2 combined with Ru(II) complexes increase the rate of TOC and COD disappearance. These is in complete agreements with the possibility of Ru(II) complexes to prevent e/h^+ recombination and therefore increase degradation rate.