



Luminescence Studies and some of Its Applications

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Abstract— Lanthanide luminescence has wide applicability in both solid and solution state luminescence studies. The process of ligand sensitized luminescence has not only enhanced the lanthanide fluorescence but also found wider applicability in the field of immunoassay and drug delivery apart from probing the site of binding or complexation. The lanthanide fluorescence enhancement not only depends on the complexing ability of the ligand but also depends on the position of the complexing/binding site. A study of the Terbium luminescence with a number of aromatic acid ligands brings out the role of the position of the carboxylic group in the aromatic ligand. The aromatic acid ligands like *b*-diketones enhance the lanthanide by nearly three orders of magnitude but use of a secondary ligand like TOPO in a micellar environment enhances further the lanthanide luminescence by another order. The complexation of lanthanide is not restricted to the simple ligands with a carboxylic group as it can complex with large molecules like DNA and in the process the DNA itself can be estimated. However here, use of TOP does not enhance any luminescence as the DNA molecule is too large to be contained within the micellar cavity to entrap the lanthanide complex. Apart from its applicability in the medical science, the lanthanide luminescence can also be applied in the industrial environment. In the power industry, the cooling water system plays a major role with respect to microbial corrosion. The sulphur reducing bacteria is a common species found in almost all the cooling water systems of India though Iron bacteria is found only in selected sites. The bacterial population is generally found through the colony counting methodology and for the first time we have reported the luminescence/fluorescence from the Iron bacteria in the cooling water system. Though the luminescence from Iron bacteria is recorded, its luminescence intensity *visa vis* its population is yet to be standardised despite the fact that the originating moiety with respect to Iron bacteria luminescence is the Tryptophan. Another important application of luminescence in recent times is in the field of Industrial Safety. The development of afterglow phosphors that emit light in absence of an exciting source for 8-10 hours has revolutionized the industrial Safety. In addition to it studies have indicated that white light emission also can be obtained from the afterglow phosphors. Another industrial application of luminescence is in the field of power plant chemistry where the flow through condenser is few meter cube of water per second. In the event of biofouling, the better way of getting practical information in the field is the measurement water flow through the condenser. However, this is an uphill task as flow meters are generally not available to measure the water flow of this magnitude and here the application luminescence is handy. This manuscript discusses the application of luminescence in all these fields.

1. LANTHANIDE FLUORESCENCE ENHANCEMENT

Fluorimetric properties of some lanthanide ions are of considerable interest in the modern day scientific and technological fields. On complexation with suitable organic ligands these ions exhibit some interesting properties. The main advantages of lanthanide chelates in fluorescence spectrometry are their large Stokes shifts, narrow emission profiles and long fluorescence lifetimes. These have led to use lanthanides as fluorescent probes for highly sensitive time-resolved Fluorimetric immunoassays, metal ion coordination in proteins and structural studies of biological macromolecules. These properties have also been used to improve the sensitivity for lanthanide estimation by conventional spectrofluorimetry and laser induced spectrofluorimetry. In aqueous medium lanthanides are weakly fluorescing species due to their low molar absorptivities and poor quantum yields. To tackle the problem due to low molar absorptivities the technique of ligand sensitized fluorescence has been used successfully. The lanthanide

fluorescence could be enhanced by several orders of magnitude by choosing proper sensitizing ligands. Notable among such ligands are thenoyltrifluoro acetone (TTA) and aromatic carboxylic acids. The poor quantum yield of lanthanide ions in aqueous solution is due to the fact that the solvent molecule itself can act as an efficient quencher. This problem has been tackled partially using synergistic ligands like trioctylphosphine oxide (TOPO) as the secondary ligands. An insulating sheath is suggested to be formed by the long alkyl chain of TOPO around the lanthanide complex, resulting in enhanced lanthanide fluorescence due to the reduced probability of collisions between solvent molecules and the lanthanide ion in the complex. Several workers have used TOPO as a synergistic ligand to enhance the lanthanide fluorescence.

The acids used were *ortho*-, *meta*-, and *para*- substituted methyl, methoxy and aminobenzoic acids along with *ortho* and *meta*-nitrobenzoic acids. Fluorescence enhancement of Tb³⁺ was seen, to a varying degree, using methyl, methoxy and aminobenzoic acids as ligands. However, Tb³⁺ fluorescence was completely quenched

with nitrobenzoic acids. The fluorescence of Tb³⁺ in the Tb³⁺-acid complexes was synergistically enhanced by the addition of trioctylphosphine oxide (TOPO) in Triton X-100. The synergism displayed by TOPO was observed only when Triton X-100 micellar medium was used. The observed synergism could be due to the energy transfer from Triton X-100 to Tb³⁺-acid complexes. In presence of SDS or DTAB micelles, no energy transfer from SDS or DTAB to Tb³⁺ was observed. Accordingly, TOPO dissolved in SDS:DTAB micellar medium did not result in synergistic fluorescence enhancement of Tb³⁺. The aromatic monocarboxylic acids studied here, together with TOPO-Triton X-100 could enhance the lanthanide fluorescence by three to four orders of magnitude. This leads to detection limits in the sub-ppb level for Tb³⁺.

In our earlier work, where we had used benzoic and trimesic acids as ligands, we found that the addition of TOPO further enhanced the fluorescence of the lanthanides in the lanthanide complexes, by another order of magnitude. However, interestingly, the pH at which maximum enhancement was observed, was different for the two ligands, benzoate and trimesate. While in the lanthanide-benzoate-TOPO system, we observed the highest enhancement near pH 6, the lanthanide-trimesate system at pH 6 showed almost no enhancement due to synergism when TOPO was added. However, when the pH was decreased to about 4, the fluorescence of the lanthanide-trimesate-TOPO system showed a maximum. In this work, we have examined this point further to see if this pH dependence is typical of all polycarboxylic acids. A variety of polycarboxylic aromatic acids were used as ligands, and some interesting aspects of fluorescence enhancement of Tb³⁺, following the addition of TOPO have emerged, which will be discussed. The aromatic acids also enhance the fluorescence of Dy³⁺ and Eu³⁺. However, because the general behaviour of the Dy³⁺ and Eu³⁺ complexes was similar to that of Tb³⁺, we have studied in detail only the Tb³⁺ complexes.

Aromatic carboxylic acids serve as excellent ligands in enhancing the fluorescence of the lanthanides Tb³⁺, Dy³⁺ and Eu³⁺. The use of these ligands resulted in an enhancement of the lanthanide fluorescence by about three order of magnitude. When these complexes were treated with TOPO-Triton X-100, these ligands behaved differently and could be classified into three groups. The monocarboxylic acids formed the first class; at pH 6 these acids showed synergism when TOPO was added. Polycarboxylic acids with no carboxyl groups ortho to each other form the second class. In these cases, addition of TOPO does show synergism, but near pH 4. In the third class, we have the polycarboxylic acids that have at least two carboxyl groups ortho to each other. In these cases we found that the addition of TOPO does not lead to any synergism at any of the pH values. Fig. 4 summarizes the pH dependence of fluorescence enhancement of Tb³⁺ following the addition of TOPO for all aromatic acids that

we have studied. The three classes have been shown separately in the figure. This study has clearly revealed the utility of aromatic carboxylic acids as ligands to sensitize the fluorescence of the trivalent lanthanides (Tb, Dy and Eu), and together with TOPO-Triton X-100 they enhance the lanthanide fluorescence by four orders of magnitude. This opens up the possibility for the use of these ligands in the Fluorimetric estimation of the lanthanides at trace levels.

2. MICROBIAL POPULATION IN COOLING WATER SYSTEM OF POWER PLANT

Fast Breeder Test Reactor (FBTR) at Kalpakkam is a 40MWt/13Mwe, sodium cooled nuclear reactor. The cooling water system (CWS) of FBTR consists of an open re-circulating type with an induced draft cooling tower and Palar river sub-soil water is used as the cooling medium. The metallurgy of CWS consists of carbon steel, copper, admiralty brass, aluminum brass, bronze, cupronickel etc. The cooling water system is treated with proprietary chemicals to minimize the corrosion and deposition in the system. Corrosion can be caused due to unfavorable water chemistry or/and due to presence of excessive microbes in the cooling water. Therefore to minimize the corrosion, addition of corrosion/scale inhibitors is essential apart from using the biocides to control the microbial population in the cooling water system. Microbiologically induced corrosion (MIC) refers to the corrosion of metals caused by micro organisms such as algae, Iron bacteria, Sulphate reducing bacteria etc. adhering to the structural material at the water-metal interfaces. To keep a tab on the microbial population, it is regularly monitored by estimating the population through various methods such as viable plate count, most probable number, membrane filtration etc. All these methods have their own advantages and disadvantages. Therefore, researchers keep trying to find out yet another better method of estimating the microbe population. In our laboratory, we have initiated studying the fluorescence of different microbes like Iron bacteria, Sulfur reducing bacteria etc. For the first time we have observed fluorescence from Iron bacteria using Spectrofluorimetry. After ascertaining the fluorescence from iron bacteria efforts were made to correlate the fluorescence intensity with the iron bacteria population. However, though our preliminary studies have confirmed the fluorescence from iron bacteria, the co-relationship between the fluorescence intensity and the iron bacteria population is yet to be established. The results of our preliminary studies are discussed here

Iron bacteria present in cooling water system of FBTR shows fluorescence with Ex/Em maxima at 280/333nm respectively. Presence of tryptophan may be the reason for iron bacteria fluorescence. With increase in colony size and time elapsed after inoculation, the fluorescence intensity is observed to be increasing.

3. STUDY WITH DNA

Research on nucleic acids has become an area of active research of life sciences due to their important functions in life processes. The natural fluorescence intensity of nucleic acids is very weak and, therefore, direct use of their fluorescence properties to study their biological properties is limited. Nucleic acids have been studied using probes such as organic dyes, metal complexes and metal ions. However, in the study of nucleic acids, lanthanide ions play an important role. These ions have been used as a probe to study the single-strand content of DNA, as a fluorescent probe for DNA and chromatin, energy transfer from RNA, etc. In the present study we have studied the fluorescence enhancement of terbium in presence of calf thymus DNA in aqueous medium.

Terbium and europium fluorescence could be enhanced by nearly two orders of magnitude in the presence of calf thymus DNA. Monitoring Tb^{3+} fluorescence, DNA could be estimated at 5 ppb. Addition of TOPO/TritonX100 did not help in enhancing the lanthanide fluorescence. Cofluorescence enhancement of Eu^{3+} was observed in presence of Gd^{3+}/Tb^{3+} and DNA.

4. CONDENSER FLOW MEASUREMENT

Condenser plays an important role in any power plant as without it the feed/steam water can not be further purified using ion exchange resins. The condenser cools the feed/steam water with the help of cooling water on the other side within the heat exchanger. However, with the use of cooling water (sea water or land water) there is always a possibility of chemical corrosion and microbial induced corrosion. Apart from these, the major concern is the biofouling of the condenser especially in case of sea water cooling. The macro foulants (organisms present in sea water) tend to deposit on the metal surface and over a period of time reduce the water flow significantly through the condenser. It is not easy to predict the extent of biofouling deposits inside the condenser as it depends on the population of macro organisms in a particular location in sea along with the water current, temperature, chlorination regime etc. Hence, the better way is get idea about the extent of biofouling is to measure the water flow through the condenser. But, it is not easy to measure this water flow as the flow is few meter cube per sec through the condenser and generally no flow meter is available to measure such a high water flow. The practical way to measure this water flow is to add some organic dye at the inlet point and detect the dye at some outlet point and either using absorption or fluorescence, the flow can be measured after noting the time at both the inlet and outlet. However, addition of any chemical to the condenser water is not preferred and if it is unavoidable, one likes to add the minimum amount which also makes sense commercially. Here, use of luminescence technique

becomes handy as the fluorescence is more sensitive than absorption technique.

Recently, this fluorescence technique was adopted Madras Atomic Power Station, Kalpakkam to estimate the water flow through four condensers to find out the biofouling effect on the condensers. It was successful in finding out the condenser with different flows which in turn was indicative of the extent of biofouling.

5. LONG GLOW PHOSPHORS

Long lasting phosphors find wide applications as display materials in different fields such as road signs, emergency exits, interior decoration, etc. These materials absorb light energy and gradually emit visible light in the absence of an excitation source for a long period of time. Among different afterglow (AGL) phosphors, europium-activated strontium aluminates like $SrAl_2O_4:Eu^{2+},Dy^{3+}$, $SrAl_4O_7:Eu^{2+},Dy^{3+}$, $SrAl_{12}O_{19}:Eu^{2+},Dy^{3+}$, and $Sr_4Al_{14}O_{25}:Eu^{2+},Dy^{3+}$ are of special interest for their efficient emission in the visible region. Different methods of phosphor synthesis are currently an active area of research with an aim to enhance the duration and intensity of the afterglow. The long after glow phosphors find a significant application in the industries from the safety point of view. In a blackout condition in an industry environment such phosphors are used as path indicators so that plant personnel can exit the industrial floor safely without coming in contact with any unwanted components. Moreover, such phosphors are very useful on road journey especially in night as these phosphors unlike the fluorescent material don't need an excitation source to glow in the night. We have synthesized $(Sr_xCa_{1-x})_4Al_{14}O_{25}:Eu^{2+},Dy^{3+}$ through solid-state reaction route. The objective was to understand the effect of mixed aluminate matrices on the afterglow.

The long AGL phosphor $Sr_4Al_{14}O_{25}:Eu^{2+},Dy^{3+}$ was successfully synthesized through the solid-state route using two different starting reactants. The intermediate products formed at different temperatures were identified as $SrAl_4O_7$ and $SrAl_2O_4$ and their PL and AGL emissions were systematically studied. The variation in PL for the samples prepared at different synthesis temperatures was due to the presence of different phases to different extent at this temperature. The observed luminescence was a convoluted emission from the different phases present. Similarly, the AGL luminescence was at different wavelengths for the samples prepared at different temperatures. Different AGL and PL were observed for the sample prepared at a temperature of $1200^\circ C$. Moreover, the AGL luminescence and PL were observed at different wavelengths for the same sample prepared at a particular temperature ($1200^\circ C$). The difference in the AGL and PL was due to differential diffusion of Eu and Dy at different temperatures. The AGL and PL emission of $Sr_4Al_{14}O_{25}$:

$\text{Eu}^{2+}, \text{Dy}^{3+}$ prepared through either route at 1200/1300°C were similar.

6. URANYL LUMINESCENCE IN SrBPO_5

Strontiumborophosphate (SrBPO_5) with and without uranium doped samples were synthesized through solid state reaction route in air atmosphere at different annealing temperatures. The dopant concentration was varied between 1 and 8 mol%. X-ray diffraction studies confirmed the formation of single phase compound in all the samples without any impurity phase up to 8 mol% of the dopant ion. The overall morphology and particle size was confirmed by scanning electron microscopic studies which suggested the presence of uneven, agglomerated particles with less than 1 μm individual size. It was observed that upon annealing at higher temperatures, the particles get agglomerated more and more with smooth boundaries. Photoluminescence (PL) studies confirmed stabilization of uranium as Uranyl ion (UO_2^{2+}) in the system. Based on the PL emission data concentration quenching was observed beyond 7 mol% of the dopant ion concentration. The critical distance (L_c) was estimated to be 3 Å suggesting Dexter type of energy transfer mechanism responsible for the quenching. The lifetime decay studies indicated the presence of two different types of environment around Uranyl ion. On annealing at temperatures beyond 900 °C the PL emission and decay time reduced drastically. It was concluded that on annealing at temperatures beyond 900 °C, defect centres get agglomerated around the metal ion providing non-radiative pathways for the energy to get dissipated thereby reducing the PL emission and

decay time. Color coordinates were evaluated for the 7 mol% uranium doped sample annealed at 900 °C. The values suggested that the system can be used as a potential green emitting phosphor material.

7. LUMINESCENCE OF Ce^{3+} ACTIVATED CALCIUM SILICATE

Rare-earth-activated CaSiO_3 was synthesized through co-precipitation technique. This phosphor exhibited broad excitation and emission in the UV region peaking at 324 and 375 nm respectively due to the $4f \rightarrow 5d$ transition in Ce^{3+} . Variation of Ca:Si ratio (x) resulted in formation of γ - Ca_2SiO_4 and β - Ca_2SiO_4 phases with significant effect on the Ce^{3+} luminescence. The fluorescence decay curves were found to be fitted well with the multi-exponential decay. The average fluorescence lifetime of the Ce^{3+} ions for x = 1, 1.43 and 2 were found to be 33.5, 34.3 and 36.5 ns respectively. The quantum efficiency of the stoichiometric phosphor was 64 %. This phosphor also exhibited intense Thermoluminescence (TL) and Optically Stimulated Luminescence (OSL). The presence of broad excitation band covering the NUV region meets the criterion of high absorption of NUV by phosphors, a necessary condition for phosphors for white LEDs based on NUV LED chips. Hence this phosphor can be explored further for the white LED applications. The phosphor also exhibit intense TL as well as OSL response. The maximum OSL sensitivity is observed for x = 2 and is found to be 62 % of that of the BARC developed $\text{Al}_2\text{O}_3:\text{C}$. The TL and OSL response was found to be linear over the range of 100 mGy to 1.2 Gy. Hence it can also be explored for the radiation dosimetry applications.