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# (54) Title: LUMINESCENT LANTHANIDE COMPLEXES AND METHOD OF PREPARATION THEREOF

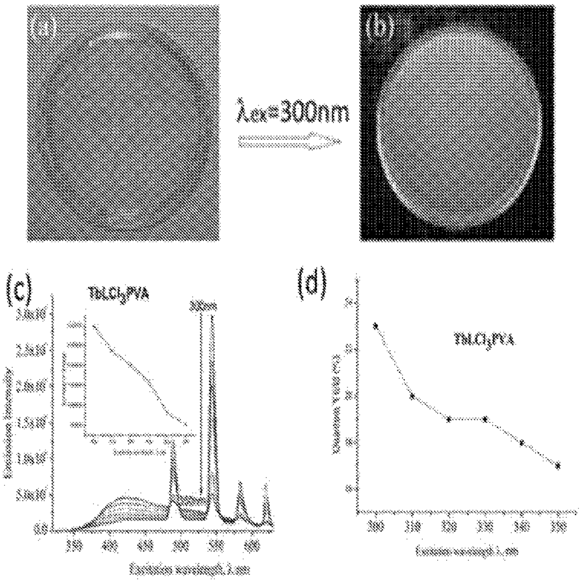

Figure 5.

(57) **Abstract**: The present invention relates to luminescent lanthanide metal based phenanthroline complexes and process for the preparation thereof. Preparation of two luminescent complexes of europium and terbium and synthesis of polymeric composite thin films by doping very low concentration of the complexes in poly vinyl alcohol (PVA) as polymer matrix is reported in the invention. Such luminescent sensor molecules are routinely used for the biomedical assay applications in the bio-chemical laboratory. The complexes are found to be an efficient phosphate and Adinosine triphosphate (ATP) sensor which possess low detection limit.

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# LUMINESCENT LANTHANIDE COMPLEXES AND METHOD OF PREPARATION THEREOF

## FIELD OF THE INVENTION

**[001]**The present invention relates to luminescent lanthanide metal based phenanthroline complexes and method of preparation thereof. Particularly the present invention relates to the preparation of two luminescent complexes of europium and terbium and synthesis of polymeric composite thin films by doping very low concentration of the complexes in poly vinyl alcohol (PVA) as polymer matrix.

**[002]** More particularly the present invention relates to use of ligand and its luminescent lanthanide metal based phenanthroline complexes in various industries working in optoelectronics, low voltage driven fluorescent lamps, optical fiber in telecommunication and data transfer, energy converter, optical sensor, display systems, laser, light emitting diode industries etc.

## BACKGROUND OF THE INVENTION

**[003]**Various luminescent materials *viz.,* light emitting diodes(LEDs), luminescent conductors, optical light transfer objects, energy converter and display objects, optical sensor, solar concentrators, low voltage driven lamps, lasers, colour inkjet etc. in particular their potentiality to generate well characterized and intense luminescence is exploited in many modern fiber optical telecommunication networks. Further such luminescent complexes have been proven for their promising application in the area of bioscience, immunoassay, bio imaging, molecular recognition and detection in low analyte level, finger printing etc. luminescent materials are generally visually unnoticeable or colorless, but develop color and become easily visible, when suitable light falls on it. Generally organic luminescent dyes are used for such purpose but their broad emissions with short life time are the disadvantage. Sharp emission, high quantum yield, long life time decay and large stokes shift shown by lanthanide complexes, rate them superior than the organic luminescent dyes. Thus lanthanide luminescent materials with above desired quality are considered as potential aiming various industries. Hence currently many leading companies all over the world are engaged in research and produce many lanthanide compounds aiming to achieve materials with above desired property. Considering the industrial demand, research and development of such lanthanide based luminescent materials are highly active worldwide and few of such related prior art which need to mention here to understand novelty of current invention are depicted below.

**[004]** References may be made to US2003060387 (A1), by Feng Lung et al., titled "Water-soluble package with luminescent dye in the film" The main drawback of the invention is a process for the preparation of PVOH based water soluble film made with only organic luminescent dye. However, lanthanide luminescent considered superior than organic dyes, the present inventions gains importance.

**[005]**Reference may be made to US6737393, by Mon-Sheng Lin titled "Liquid bubble solution for producing Luminous bubbles" The main drawback of the invention is that it uses liquid bubble composed with water surface active agents and glycerin was mixed with fluorescent brightening agents. In this invention the bubbles are illuminated in dark by external sources of UV or IR radiation. This invention thus fails to use any lanthanide luminescent complexes.

**[006]**Reference may be made to US5106957, by Ron-L-Hale et al., titled "Fluorescent Poly(arylpyridine) rare earth chelators". The main drawback of the invention is that the patent reveals a series of Poly(arylpyridine) ligand comprising transition metal or rare earth metal ions, highlights that these compounds are fluorescent. This patent has not provided any information about life time and quantum yield. Further this patent discloses a series of organic fluorescent dye type chelates and the investigation on their rare earth metal based fluorescent properties was not carried out.

**[007]**Reference may be made to US5435937, by Colin D Bell et al., titled "Fluorescent compounds" presents a series of transition metal, lanthanum and actinide complexes. This patent reports $Eu(DBM)_3$ where DBM = dibenzylmethane and radioactively labelled polymeric materials to work in the radioactive environment. The main drawback of the invention is that the emission was observed in the UV radiation and in shorter wavelength which includes ionizing radiation. Thus this invention fails to investigate the longer wavelength of visible region which harmless.

**[008]**Reference may be made to US5512493, by Gerard Mathis et al., titled “Method of amplifying the emission signal of a luminescent compound” describes assay method for the detection of various bio-analytes using europium cryptate Eu-tris(bippyridine) (EuTBP) and the compound has been excited at 307nm and not beyond that. This study gives method for the detection of bioanalytes and some photophysical measurements. However this compound although being luminescent, the main drawback of the invention is that the film fabrication has not been investigated and this study has been limited only to solution state investigation.

**[009]**Reference may be made to RU2478682C1, by Dushenko Galina et al., titled “Luminescent coordination compounds of lanthanides for light emitting diodes” wherein the patent discloses more about the synthesis and characterization of phenanthroline based lanthanide complexes. The main drawback of the invention is that it does not reveal anything about the film fabrication.

**[010]**Reference may be made to a paper published by J.C.G. Bunzli et al., Journal of Rare Earths 28, 2010 pp 824-842, illustrates various potential application of lanthanide luminescent properties. The main drawback of the invention is the synthesis of the diketone ligand is highly complex; secondly the reported tetrakisdiketone Eu(III) complex with $Na^+$ as counter ion exhibits very low quantum yield; although this complex has been reported to be excited in the wide range of 254-500nm, the quantum yield is very low 0.28 % at 350nm excitation.

**[011]**Reference may be made to US7736620, by Tetsuji Moriguchi Kitakyushu titled “Europium diketone chelate compounds and fluorescent material using the same. The reported tetrakisdiketone Eu(III) salt formation with positive species such as $Na^+$, polyvinylpyridine etc., has been excited only at UV wavelength ranging 254-365nm. The drawback of this compound is that it is insoluble in water and soluble in polar protic solvents such as dimethylsulphoxide (DMSO), dimethylformamide (DMF), N-methyl- pyrrolidone (NMP), methanol, ethanol and isopropanol.

**[012]** Reference may be made to RU2499022 entitled “Europium tris[1-(4-(4-propylcyclohexyl)phenyl)decane-1,3-diono]-[1,10-phenathroline] as luminescent material”. A series of diketone derivatives were synthesized and used as antenna for Eu(III) metal. This Eu-complexes were irradiated with $\lambda_{max}$ = 337nm in solid state.

However the Eu polymer matrix fabricated in this invention is less efficient than the present polymeric matrix such as water solubility, lower energy excitation with high output and many fold high luminescent intensity, warrants the present complex to be patented.

**[013]** Reference may be made to a paper by M.L.P. Reddy et al., in Journal of Material Chemistry 2012, 22, 10852-10859, wherein, Europium complex made with Polymethylmethacrylate (PMMA) produce comparatively less quantum yield, while the respective Tb(PMMA) polymeric film provide 52%. Thus both these luminescent films made with PMMA are inferior to our present invention in view of the quantum yield. The main drawback of the invention is that film reported here are insoluble in water and soluble in organic solvents such as dichloromethane (DCM), dimethylsulphoxide (DMSO). The films are not biodegradable.

**[014]** References may be made a paper published by Carmen Coya and coworkers (Journal of luminescence 159(2015) pp17-25) illustrates a highly luminescent red emitting fluorinated β-diketonate, octacordinated Eu(III) complex $[Eu(cbtfa)_3(bath)]$ reported as efficient energy transfer Q = 60% in crystalline powder and Q = 50% in thin film with thermal stability upto 200°C. This film is reported to dissolve in $CHCl_3$ and are not tested for their solubility in water. In view of life time decay. In film $\tau_{obs} = 620\mu s$. Further this film was excited using wavelength 270nm.

**[015]** References may be made Plannel's et al (Eur. J. Inorg Chem., 2014, pp 3095-3100) where the $[Eu(hfac)_3 (H_2O)_2]$ where hfac = hexafluroacetylacetaeto doped in PVA is reported. Although their polymeric film is water soluble the quantum yield(Q) is achieved only 30%.

**[016]**In view of the above understanding, the present complex **EuLCl$_3$** and **TbLCl$_3$** deserves importance due to its complete solubility in water, Since water is an ecofriendly, environmentally benign solvent, it is an added advantage. Thus both these complexes giving excellent luminescence, this complexes are considered to deserve various diversified potential application in the area of bioassay, molecular recognition etc. Further, the thin film with thickness ranging 0.12 ± 0.02mm shows enhanced relative quantum yield ranging 181-35% in their respective excitation wavelength from

360-430nm. Further this **$EuLCl_3PVA$** film material showed enhanced life time decay ranging 0.730 ± 0.01ms, while the respective **$TbLCl_3PVA$** has been enhanced into 1.15 ± 0.01ms. In addition to this both these complexes **$EuLCl_3$** and **$TbLCl_3$** are tested for their sensing property and found that these complexes are highly selective towards Phosphate/ATP and their low detection limit (LOD) was achieved upto 0.02μM of ATP (adenonise triphosphate) at pH = 7.4 using water as solvent.

## OBJECTS OF THE INVENTION

**[017]**The main object of the present invention is a ligand and its luminescent lanthanide complexes which are used for the preparation of luminescent film.

**[018]** Another object of the present invention is synthesis of luminescent lanthanide complexes **$EuLCl_3$** and **$TbLCl_3$** and its composite films. The thin films with thickness 0.12 ± 0.02 mm, exhibits relative quantum yield ($\Phi_{rel}$) in the range of 181-35% in their respective excitation wavelength from 360-430 nm. Further the **$EuLCl_3PVA$** film material emitting “brilliant red emission” possess life time decay 0.730 ± 0.01ms; Similarly the other film **$TbLCl_3PVA$** possess long life time decay 1.15 ± 0.01ms.

**[019]** Yet another object of the present invention is to design and develop luminescent lanthanide complex which absorbs UV.

**[020]** Yet another object of the present invention is to convert the UV light into visible light by using this lanthanide based material.

**[021]** Yet another object of the present invention is to use low energy wavelength in the visible range for excitation and emission also at visible range.

**[022]** Yet another object of the present invention is to obtain water soluble luminescent complex and its luminescent films

**[023]** Still another object of the present invention is to prepare a thin film with enhanced relative quantum yield and long lifetime.

**[024]** Still another object of the present invention is to prepare a thin film which function as optical sensor and convert light from UV and visible range wavelength into visible range.

**[025]** Still another object of the present invention is to prepare a thin film which emits brilliant red luminescence on absorbing visible range wavelength upto 430nm.

**[026]** Still another object of the present invention is that the polymeric matrix synthesized must be cheap, biodegradable and nontoxic.

**[027]** Still another object of the present invention is that the Eu and Tb complexes are luminescent active at pH range 6.5 to 9.0.

**[028]** Still another object of the present invention is that the europium and terbium complexes are stable at pH 7.4.

**[029]** Still another object of the present invention is that the said luminescent complex **$EuLCl_3$** and **$TbLCl_3$** are found to be an efficient phosphate and Adinosine triphosphate (ATP) sensor which possess low detection limit (LOD) 0.2μM at pH = 7.4.

**[030]** Another object of the present invention is to achieve a high distribution of luminescent metal in the polymeric matrix.

## [031]BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 depicts TEM images (a) Eu PVA and (b) TbPVA film. The spots in it shows the population of Eu and Tb elements in the PVA matrix.

Figure 2 depicts life time decay 2(a) depicts monoexponential life time decay observed for complex $EuLCl_3$ and $TbLCl_3$ in solution state and 2 (b) depicts monoexponential life time decay observed for PVA film doped with $EuLCl_3$ and $TbLCl_3$.

Figure 3 depicts low detection limit titration performed with (a) $EuLCl_3$ and (b) $TbLCl_3$ against ATP (pH = 7.4).

Figure 4 depicts (a) Transparent film of $EuLCl_3PVA$ in absence of optical source and (b) in presence of optical source (λex = 360nm) turning into brilliant red luminescence. (c) Emission spectra recorded at different excitation wavelengths ranging 360- 430 nm. d). % of relative Quantum Yield at different excitation wavelength ranging 360 - 430nm.

Figure 5 depicts (a) Transparent film of $TbLCl_3PVA$ in absence of optical source (b) in presence of optical source (λex = 300nm) turning into bright green. (c) Emission spectra recorded at different excitation wavelengths ranging 300 – 350nm. (d). % of relative Quantum Yield at different wavelength ranging 300-350nm.

Figure 6 depicts the thermogravimetric analysis (Thermal stability of the film upto 220°C).

Figure 7 depicts powder XRD pattern of the PVA film made of doping complex $EuLCl_3$ and $TbLCl_3$.

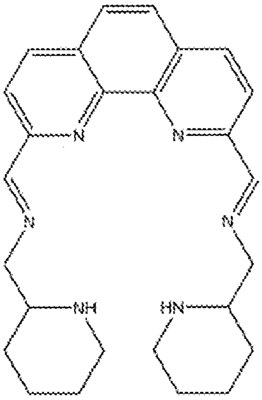
## SUMMARY OF THE INVENTION

**[032]** The present invention provides a lanthanide complex of formula $LnLCl_3.(H_2O)_n$ wherein

Ln is selected from Eu or Tb

n= 3 or 4

**L** =



## DETAILED DESCRIPTION OF THE INVENTION

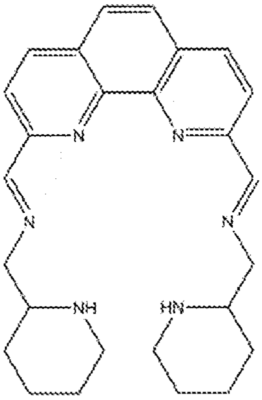
**[033]**Accordingly, the present invention provides a lanthanide complex of formula $LnLCl_3.(H_2O)_n$

wherein

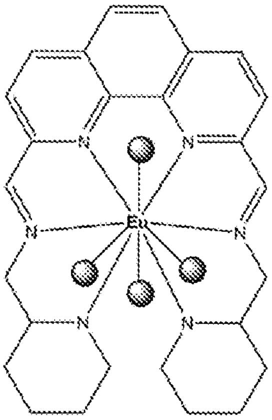
Ln is selected from Eu or Tb

n= 3 or 4

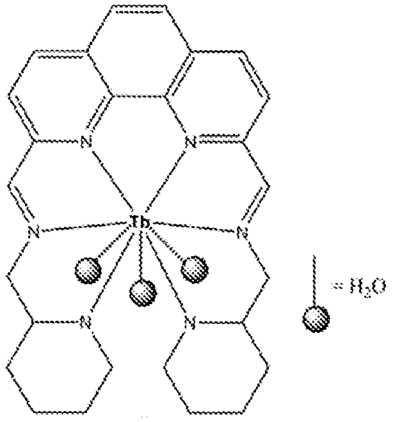
**L** =



**[034]** In an embodiment of the present invention, representative complex comprising



**1a**



**1b**

**[035]** In another embodiment, present invention provides a process for the preparation of lanthanide complex of formula $LnLCl_3.(H_2O)_n$ and the said process comprising the steps of:

i. dissolving 50 to 55wt% 1,9-diformyl-1,-10-phenanthroline in alcoholic solvent to obtain a solution;

ii. dissolving 45 to 50 wt% of 2-(Aminomethyl)piperidine in alcoholic solvent to obtain a solution;

iii. adding solution as obtained in step (i) to the solution obtained in step (ii) followed by stirring for period in the range of 40-55 hrs at temperature in the range of 30°C to 50°C to obtain ligand L;

iv. dissolving the ligand L as obtained in step (iii) in solvent to obtain a solution;

v. dissolving metal salt ($LnCl_3$) in solvent to obtain a solution;

vi. adding solution as obtained in step (iv) to the solution as obtained in step (v) followed by stirring for period in the range of 2 to 6 hrs at temperature in the range of 20°C to 30°C to obtain lanthanide complex.

**[036]** In yet another embodiment of the present invention, solvent used is alcohol, preferably methanol.

**[037]** In still another embodiment of present invention, the said complex is useful for the preparation PVA film of formula $LnLCl_3PVA$ and the said process comprising the steps of:

i. doping lanthanide complex in aqueous solution of poly vinyl alcohol (PVA) followed by stirring and casting on polypropylene plates to obtain PVA film of formula $LnLCl_3PVA$.

**[038]** In still another embodiment of the present invention, thickness of the said film is in the range of 0.12 ± 0.02mm.

**[039]** In yet another embodiment of the present invention, the relative quantum yield of obtained PVA film of formula $LnLCl_3PVA$ is in the range of is in the range of 17-181% in their respective excitation wavelength from 430-300nm.

**[040]** In still another embodiment of present invention, the life time decay of obtained PVA film of formula $LnLCl_3PVA$ is 1.15 ± 0.01ms.

**[041]** In still another embodiment of present invention, the said complex are found to be an efficient phosphate and Adinosine triphosphate (ATP) sensor which possess low detection limit (LOD) 0.2 - 0.4μM at pH ranging of 7.4.

## EXAMPLES

**[042]** Following examples are given by way of illustration and therefore should not be construed to limit the scope of the invention.

**[043] EXAMPLE 1**

**Synthesis of Ligand L**

1,9-diformyl-1,-10-phenanthroline (0.001 mmol, 0.200g) was dissolved in 50mL of $CH_3OH$. To this methanolic solution, 2-(Aminomethyl)piperidine (0.002 mmol, 0.184g) was added drop by drop. This reaction mixture was stirred continuously for 48 h at 50 °C. During this, the reaction mixture changing from colourless to reddish brown, indicates the formation of Schiff base. The solvent was removed under vacuum and the resultant orange–red powder was isolated.

-Yield. 70%. -$^1H$ NMR ($CDCl_3$, 500.130MHz): $\delta$ = 8.26, 8.24(*dd*, *J* = 3Hz, 2H), 7.86,784,7.82(*t*, *J* = 10Hz, 4H), 7.77(*s*, 2H), 3.55(*brs*, 2H), 3.27(*m*, 2H), 3.09, 3.07, 3.05, 3.03 (*q*, *J*=10Hz, 2H), 2.83, 2.81, 2.79 (*t*, *J* = 12Hz, 2H), 2.50(*m*, 2H), 2.24, 2.22, 2.20(*t*, *J* = 11Hz, 2H), 1.93-1.83 (*dd*, *J* = 12Hz, 4H), 1.60-1.50(*m*, 6H), 1.34-

1.31(*m*,2H). -$^{13}$C[$^{1}$H] NMR, 125.757 MHz) δ = 160.22, 145.27, 136.89, 128.66, 126.30, 122.75, 122.64, 83.14, 83.06, 64.20, 50.66, 48.99, 28.64, 24.91, 23.95. -DEPT-135°($CDCl_3$, 500.130MHz, δ). 131.59, 121.00, 117.44, 117.34, 77.85, 58.93 (CH, up), 45.40, 43.72, 23.37, 19.64, 18.68($CH_2$, down). -UV vis ($CH_3OH$, nm (ε, M$^{-1}$ cm$^{-1}$)): λ = 275 (32170), 234(31530); ESI[MS]$^{+}$: m/z (calc (found)) 429.28 (429.69 for M+H$^{+}$); 451.26 (451.69 for M+Na$^{+}$). Calc (found) for $C_{26}H_{32}N_6.4H_2O$: C 62.38(62.44), H 8.05(7.74), N 16.79(16.22) %.

**[044] EXAMPLE 2**

**Synthesis of complex $EuLCl_3$**

The methanolic solution of ligand L (0.054g, 0.1mmol) and $EuCl_3$ salt (0.046g, 0.1mmol) were mixed together and allowed for constant stirring at room temperature for 4hrs. After completion of the reaction, the solution was evaporated and the solvent was removed under vacuum. The resultant light brown powder was isolated.

Yield. 75%. IR (KBr): $\nu$ cm$^{-1}$ = 3398(br), 1623(s), 1458(m), 1432(m) 1400(s), -UV vis (HEPES Buffer, pH 7.4, nm (ε, M$^{-1}$ cm$^{-1}$)): λ=237(21392), 285(20212); ESI-MS$^{+}$: m/z (calc (found) 687.10 (687.12) for $[EuL(Cl)_3.H^+]^+$; 651.13(651.15) for $[EuL(Cl)_2{\cdot}H^+]^{2+}$

**[045] EXAMPLE 3**

**Synthesis $EuCl_3$PVA film fabrication**

The methanolic solution of ligand L and $EuCl_3$ salt were mixed together and allowed for constant stirring at room temperature. After completion of the reaction, the solution was evaporated and the solvent was removed under vacuum. The resultant light brown powder was isolated. A stock solution of Poly vinyl alcohol (PVA) was prepared dissolving in 100mL of water. 0.5mL of $EuLCl_3$ ($1x10^{-3}$ M) solution was doped in 10mL of transparent PVA solution. Both these compounds were thoroughly mixed upon stirring and the resultant mixture called "slime" was casted on polypropylene plates. Leaving this slime at room temperature in open atmosphere provide a transparent, smooth and colorless thin film with 0.12±0.02mm thickness (Figure 4a).

**[046] EXAMPLE 4**

**Synthesis of Complex $TbLCl_3$**

The methanolic solution of ligand L (0.054g, 0.1mmol) and $TbCl_3$ salt (0.046g, 0.1mmol) were mixed together and allowed for constant stirring at room temperature for 4hrs. After completion of the reaction, the solution was evaporated and the solvent was removed under vacuum. The resultant light brown powder was isolated.

–Yield. 65 %. IR (KBr): ν $cm^{-1}$ = 3432(br), 1627(s), 1459(m), 1432(m) 1390(s). -UV vis (HEPES Buffer, pH 7.4, nm (ε, $M^{-1}$ $cm^{-1}$)): λ=236(215725), 285(13917); ESI-MS: m/z (calc(found)) 693.11.(693.09) for $[TbL(Cl)_3.H^+]^+$; 657.13(657.12) for $[TbL(Cl)_2.H^+]^{2+}$.

## [047] EXAMPLE 5

### Synthesis of $TbCl_3$PVA film fabrication

The methanolic solution of ligand L and $TbCl_3$ salt were mixed together and allowed for constant stirring at room temperature. After completion of the reaction the solution was evaporated and the solvent was removed under vacuum. The resultant light brown powder was isolated. Stock solution of Poly vinyl alcohol (PVA) dissolved in 100mL of water was prepared. 0.5mL of $TbLCl_3$ ($1x10^{-3}$M) solution was doped in 10mL of transparent poly vinyl alcohol (PVA) solution. Both these compounds were thoroughly mixed upon stirring and the resultant mixture called “slime” was casted on polypropylene plates. Leaving this slime at room temperature in open atmosphere provide a transparent, smooth and colorless thin film with 0.12±0.02mm thickness. (Figure.5a)

## [048] EXAMPLE 6

### Luminescent Film and its optical properties

The lumiphore is phenanthroline and piperidine based hexadentate ligand (L) and the metal belongs to lanthanide elements such as europium (III) or terbium (III). The complex **1**, $EuLCl_3$ is comprised with the lumiphore *i.e.,* Phenanthroline and piperidine based ligand and europium(III) chloride. Complex **2,** $TbLCl_3$ is composed with $TbCl_3$ and the same lumiphore This complex **$EuLCl_3$** emits metal centered “red emission” at 614nm by absorbing UV source (λex) of 280nm in their solution state and the respective relative quantum yield was estimated as $\Phi = 3.9\%$ with respect to quinine sulfate and their lifetime decay was established as $\tau = 0.20$ms.

Similarly the complex **$TbLCl_3$** with Tb(III) ion emits intense “green emission” at 545nm by absorbing 280nm ($\lambda$ex) of UV radiation in its aqueous solution state and the respective relative quantum yield and lifetime decay was measured as $\Phi = 0.4.\%$ and $\tau = 0.21$ms . The lanthanide complex emits monochromatic light with 8±2 nm half width by absorbing UV light in the range 280nm in its solution state. Both these complexes provides very low relative quantum yield ($\Phi$rel = 3.9% (**$EuLCl_3$**), $\Phi$rel = 0.4% (**$TbLCl_3$**)) and lifetime decay ($\tau_{obs}$ = 0.20(**$EuLCl_3$**), $\tau_{obs}$ = 0.21(**$TbLCl_3$**)] in their respective solution state (Figure 2).

However with an aim to increase the quantum yield and lifetime, a series of composite luminescent thin films were fabricated adapting polymeric matrix polyvinylalcohol (PVA) as shown in Figure 4a & Figure 5a. Accordingly a composite thin film was fabricated by doping 0.5mL of $1x10^{-3}$M of complex **$EuLCl_3$** and **$TbLCl_3$** in PVA. Thus the resultant thin films **$EuLCl_3PVA$** and **$TbLCl_3PVA$** fabricated shows highly enhanced luminescent property. This film exists as colourless, transparent and the thickness was measured as 0.12 ± 0.02 mm and possess high mechanical stability and flexibility. Further this thin film **$EuLCl_3PVA$** exhibits steady and stable “brilliant red emission” at room temperature by absorbing wide range of excitation light ranging Ultraviolet *i.e* 280nm to visible light 430nm. Using quinine sulfate as reference compound ($\Phi$ref = 0.54), the relative quantum yield measured for this **$EuLCl_3PVA$** thin film, showed 91% by absorbing 370nm. A similar excitation process carried out at 360 nm providing, relative quantum yield ($\Phi$rel) as 181%, a further decrease in the excitation wavelength moving from 350-280 nm, provides a very strong red emission at 614nm.

## [049] ADVANTAGES OF THE INVENTION

1. It is recognized that the synthesis of the complexes **$EuLCl_3$** and **$TbLCl_3$** and the films **$EuLCl_3PVA$** and **$TbLCl_3PVA$** are simple, low cost and economically cheap and water soluble.

2. The lanthanide complexes show sharp emission, high quantum yield, and long life time decay and large stokes shift (254nm) compared to organic fluorescent dyes.

3. The complexes **$EuLCl_3$** and **$TbLCl_3$** are luminescent at room temperature and are highly soluble in water and stable at physiological pH 7.4.

4. It is further recognized that both the complexes are soluble in water and therefore can be used for bioassay studies in biomedical tests.

5. It is further recognized that both these complexes **$EuLCl_3$** and **$TbLCl_3$** being water soluble they work as phosphate sensor.

6. It is recognized that these complexes **$EuLCl_3$** and **$TbLCl_3$** being highly selective towards ATP the low detection limit (LOD) is achieved upto 0.2μM of ATP (adenosine triphosphate) at pH = 7.4. (Figure 3)

7. It is also recognized that the composite films have high mechanical strength and transparency and have smooth surface.

8. It is recognized that both these films are highly thin with 0.12±0.01mm thickness.

9. It is recognized that the composite films fabricated doping **$EuLCl_3$** and **$TbLCl_3$** are highly luminescent and the film **$EuLCl_3PVA$** emits "brilliant red emission" while the film **$TbLCl_3PVA$** emits "green emission".

10. It is recognized that the film **$EuLCl_3PVA$** can be excited at wide range of energy covering ultra-violet band of visible band. *i.e.,* 280-390nm in the UV range; in the visible range from 400 to 430nm. (Figure 4c and Figure 4d)

11. It is recognized that the film **$TbLCl_3PVA$** can be excited at 280-350nm using UV range.

12. Relative quantum yield achieved for the film **$EuLCl_3PVA$** is 91% absorbing 370nm; while $\Phi_{rel} = 181\ \%$ is with $\lambda ex = 360nm$ is established (Figure 4d).

13. It is also recognized that the polymeric materials transfer optical energy with highest efficiency.

14. It is also recognized that the polymeric films made up of PVA are nontoxic and biodegradable.

14. It is also recognized that both these films are thermally stable upto 220°C. (Figure 6)

15. The receptive nature of the PVA film of both **$EuLCl_3$** and **$TbLCl_3$** are high as evidenced from TEM analysis in the polymeric matrix. (Figure 1).

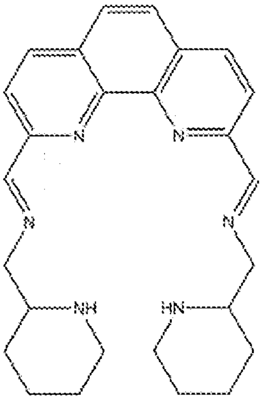
## We claim

1. A lanthanide complex of formula $LnLCl_3.(H_2O)_n$

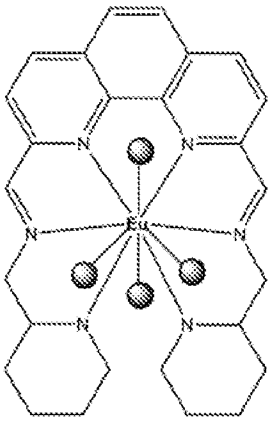
   wherein Ln is selected from Eu or Tb

   n= 3 or 4

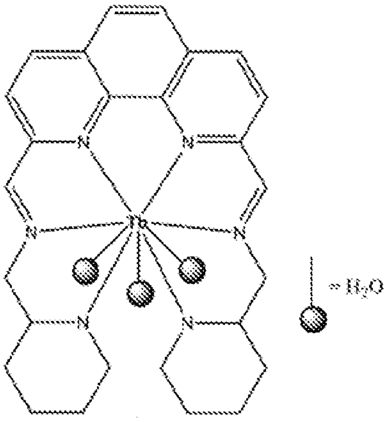
   **L** =



2. The complex as claimed in claim 1, wherein representative complex comprising



**1a**



**1b**

3. A process for the preparation of complex as claimed in claim 1, wherein said process comprising the steps of:

   i. dissolving 50 to 55 wt% 1,9-diformyl-1,-10-phenanthroline in alcoholic solvent to obtain a solution;

   ii. dissolving 45 to 50 wt% of 2-(Aminomethyl)piperidine in alcoholic solvent to obtain a solution;

iii. adding solution as obtained in step (i) to the solution as obtained in step (ii) followed by stirring for period in the range of 40-55 hrs at temperature in the range of 30°C to 50°C to obtain ligand L;

iv. dissolving the ligand L as obtained in step (iii) in solvent to obtain a solution;

v. dissolving metal salt ($LnCl_3$) in solvent to obtain a solution;

vi. adding solution as obtained in step (iv) to the solution obtained in step (v) followed by stirring for period in the range of 2 to 6 hrs at temperature in the range of 20°C to 30°C to obtain lanthanide complex.

4. The process as claimed in claim 3, wherein solvent used is alcohol, preferably methanol.
5. The complex as claimed in claim 1, wherein the said complex is useful for the preparation PVA film of formula $LnLCl_3PVA$ and the said process comprising the steps of:
   i doping lanthanide complex in aqueous solution of poly vinyl alcohol (PVA) followed by stirring and casting on polypropylene plates to obtain PVA film of formula $LnLCl_3PVA$.
6. The PVA film as claimed in claim 5, wherein the thickness of obtained PVA film of formula $LnLCl_3PVA$ is in the range of $0.12 \pm 0.02$mm.
7. The PVA film as claimed in claim 5, wherein the relative quantum yield of obtained PVA film of formula $LnLCl_3PVA$ is in the range of is in the range of 17-181% in their respective excitation wavelength from 430-300nm.
8. The PVA film as claimed in claim 5, wherein the life time decay of obtained PVA film of formula $LnLCl_3PVA$ is $1.15 \pm 0.01$ms.
9. The complex as claimed in claim 1 and 2, wherein the said complexes are found to be an efficient phosphate and Adinosine triphosphate (ATP) sensor which possess low detection limit (LOD) 0.2 - 0.4μM at pH ranging of 7.4.

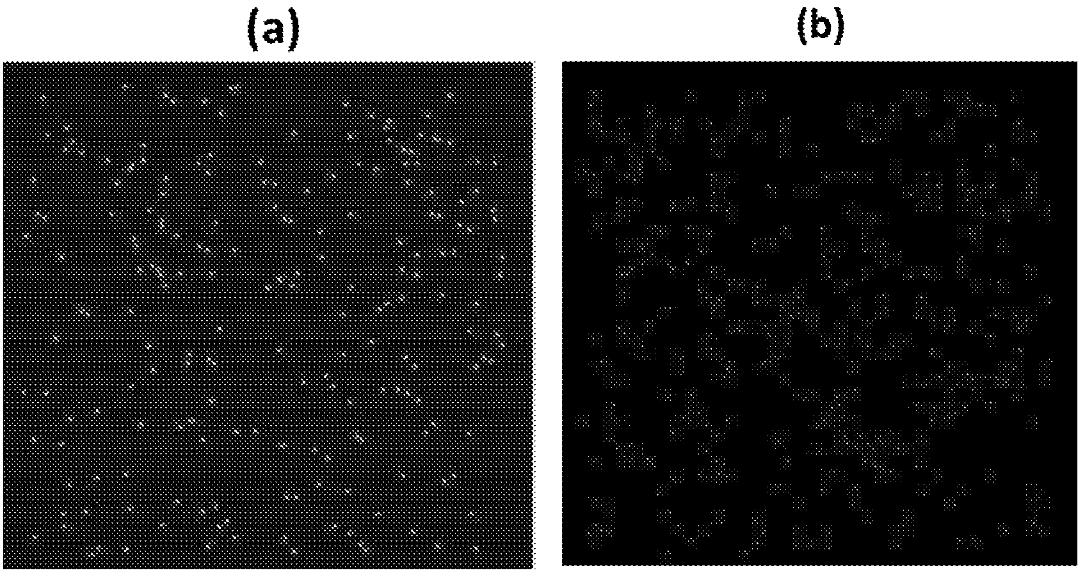


Figure 1

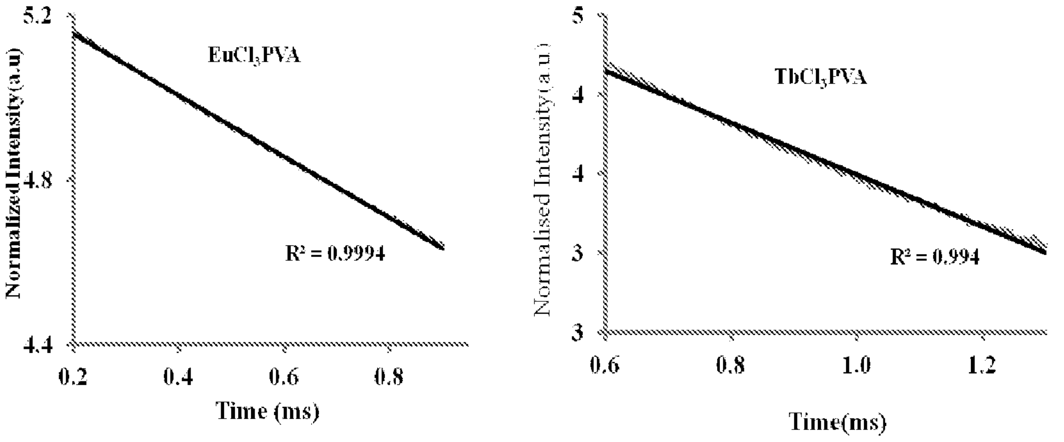


Figure 2

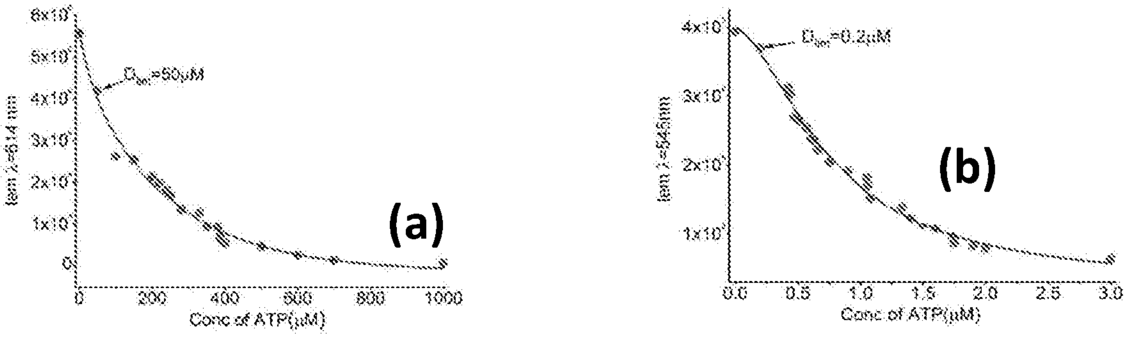


Figure 3.

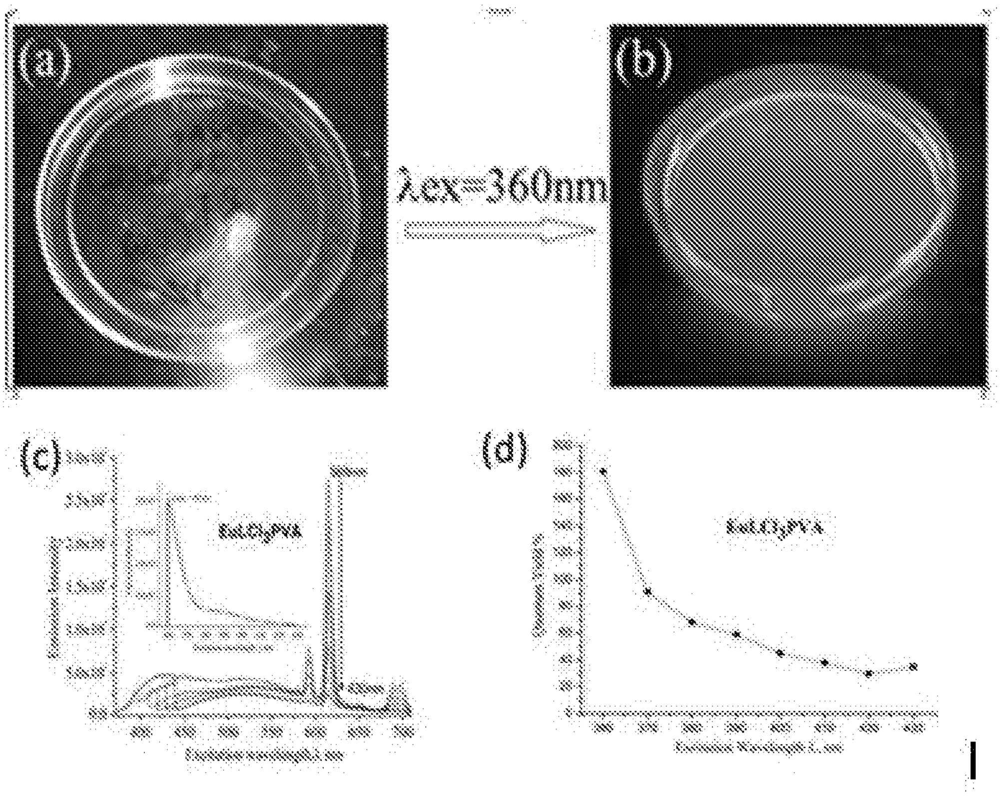


Figure 4.

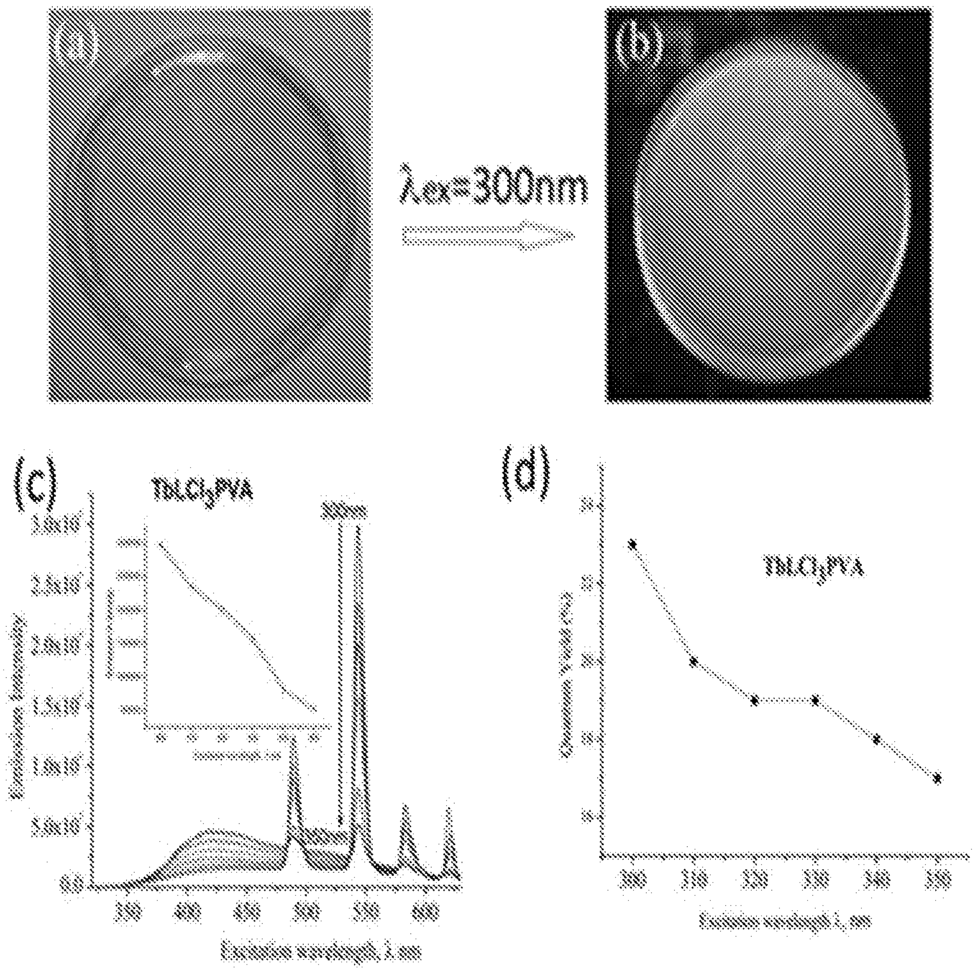

(a)
(b)
λex=300nm
(c)
TbCl3PVA
300nm
3.0x10
2.5x10
2.0x10
1.5x10
1.0x10
5.0x10
0.0
350
400
450
500
550
600
Excitation wavelength, λ nm
(d)
TbCl3PVA
300
310
320
330
340
350
Excitation wavelength λ, nm

Figure 5.

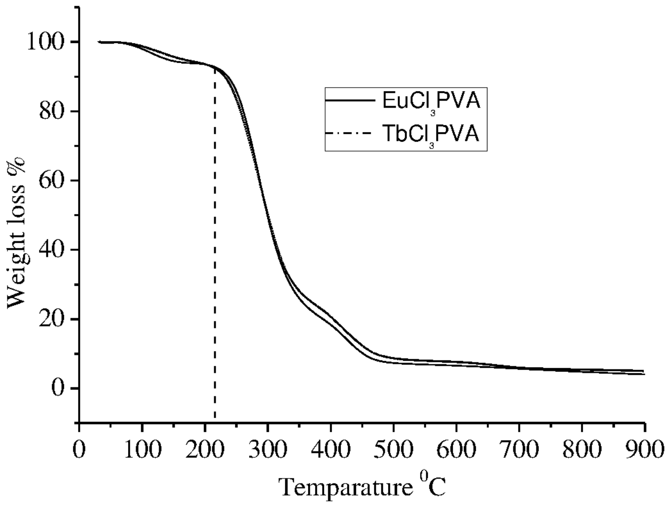


**Figure 6.**

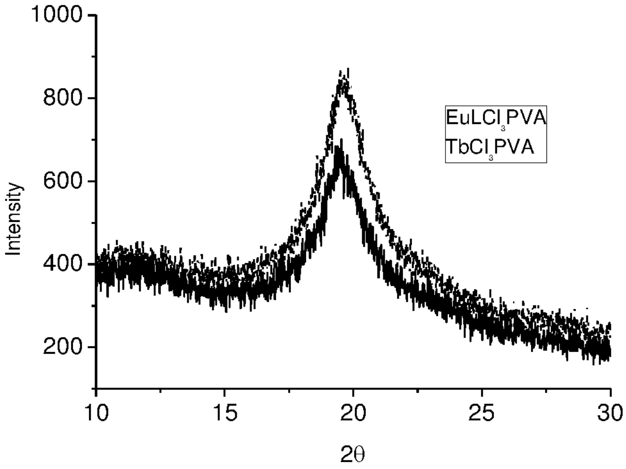


**Figure 7.**

# INTERNATIONAL SEARCH REPORT

International application No
PCT/IN2015/050144

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09K11/02 C09K11/06 C12Q1/00
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C09K C12Q

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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|---|---|
| Date of the actual completion of the international search<br>22 February 2016 | Date of mailing of the international search report<br>29/02/2016 |
| Name and mailing address of the ISA/<br>European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040,<br>Fax: (+31-70) 340-3016 | Authorized officer<br>Pötzsch, Robert |

1

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/IN2015/050144

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
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| | | US 2009136931 A1 | 28-05-2009 |
| | | WO 2007026808 A1 | 08-03-2007 |