



(43) International Publication Date
11 February 2016 (11.02.2016)

- (51) International Patent Classification:
G01N 21/64 (2006.01) *B82Y 15/00* (2011.01)
- (21) International Application Number:
PCT/IN2015/050082
- (22) International Filing Date:
6 August 2015 (06.08.2015)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
2228/DEL/2014 6 August 2014 (06.08.2014) IN
- (71) Applicant: COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH [IN/IN]; Anusandhan Bhawan, Rafi Marg, New Delhi 110 001 (IN).
- (72) Inventors: LUWANG, Meitram Niraj; National Chemical Laboratory, Dr. Homi Bhabha Road, (Maharashtra) Pune-411008 (IN). GHOSH, Debasish; National Chemical Laboratory, Dr. Homi Bhabha Road, (Maharashtra) Pune-411008 (IN).
- (74) Agent: SINGH, Manisha; Lexorbis, 709/710, Tolstoy House, 15 – 17, Tolstoy Marg, New Delhi 110001 (IN).
- (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT,

HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

- (84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))
- as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))

Published:

- with international search report (Art. 21(3))
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))

(54) Title: PARA-AMINO BENZOIC ACID SENSITIZED TERBIUM DOPED LAF₃ NANOPARTICLES FOR DETECTION OF EXPLOSIVE NITRO COMPOUNDS

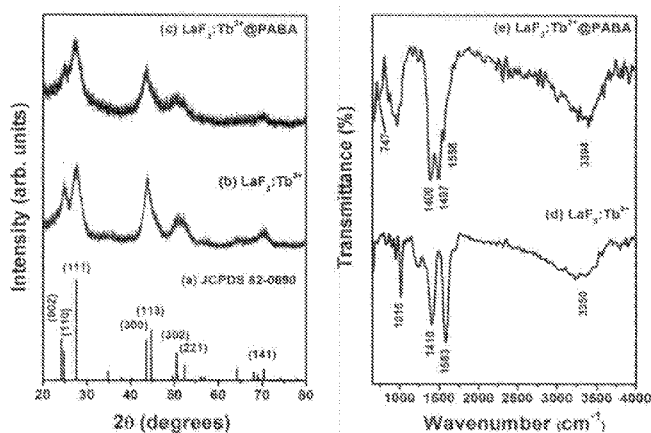


Figure 1

(57) Abstract: The patent relates to para amino benzoic acid (pABA) sensitized terbium (Tb³⁺) doped spherical LaF₃ nanoparticles used for detection of nitro group containing compounds using the terbium (Tb³⁺) doped spherical LaF₃ nanoparticles sensitized by para amino benzoic acid (pABA).

**PARA-AMINOBENZOIC ACID SENSITIZED TERBIUM DOPED LaF₃
NANOPARTICLES FOR DETECTION OF EXPLOSIVE NITRO COMPOUNDS**

FIELD OF THE INVENTION

5 The present invention relates to the para amino benzoic acid (pABA) sensitized terbium (Tb³⁺) doped spherical LaF₃ nanoparticles for detection of nitro compounds. Particularly, present invention relates to a method for the detection of highly explosive nitro compounds using the terbium (Tb³⁺) doped spherical LaF₃ nanoparticles sensitized by para amino benzoic acid (pABA).

10 BACKGROUND OF THE INVENTION

 Explosive materials are generally reactive substances which have a great amount of potential energy that can give an explosion accompanied by light, heat, sound and pressure. Among the explosive materials, nitro compounds like 2,4-dinitrotoluene (2,4-DNT), 2,4,6-trinitrotoluene (TNT), 1,3,5-tinitroperhydroxo-1,3,5-tetrazine (RDX), etc are some of the generally used components. Apart
15 from being used as an explosive material, nitro compounds like TNT are hazardous to human health which can cause various health concerns like anemia, abnormal liver function, etc. Considering the hazardous nature of the nitro compounds in terms of both security concerns and as a pollutant, the need for the detection of these materials has been the primary importance.

 Researchers all over the globe have been working on various techniques for the detection of
20 explosive material. Some of the known techniques are metal detectors which generally detect metal based weapons, canines with their superior sensing capabilities, X-ray machines by analyzing the density of the materials, neutron activation where the explosive materials is bombarded with neutrons which gives its elemental composition, and so on. Apart from the above mention techniques, spectroscopic techniques especially fluorescence based chemo sensors, due to their high sensitivity
25 and probability of using as a hand held devices for in-field detection have superior advantage. Generally, in this approach, the fluorescent materials on interaction with the explosives materials either turn-off or quenches the luminescent of the sensors which relies on an oxidative quenching mechanism. In detail, the sensor material plays the role of an electron donors and aromatic nitro compounds as an electron acceptor due to the presence of their electron withdrawing nitro groups. On
30 excitation with photon, an electron is transferred from the sensor materials to the analyte, leading to oxidation of the excited state, thereby quenching the fluorescence of the sensors. Some of the generally used fluorescent materials are conjugated polymers, metal complexes, dendrimers, carbon nanotubes, and recently the use of metal organic framework (MOF) as the new generation of sensors materials for explosive detection.

35 Article titled, "Enhanced emission of ultra-small-sized LaF₃:RE³⁺ (RE = Eu, Tb) nanoparticles through 1,2,4,5-benzenetetracarboxylic acid sensitization " by Suwen Li et. al in Nanoscale, 2012,4, 5619-5626 reports that uniform, ultra-small-sized and well-water-dispersible LaF₃ nanoparticles

doped with trivalent rare earth (RE) ions (Eu^{3+} or Tb^{3+}) have been synthesized by a simple, low temperature synthesis route. The nanoparticles, with sizes of about 3.2 nm (for those doped with Eu^{3+}) and 3.0 nm (for those doped with Tb^{3+}), are roughly spherical and monodisperse. 1,2,4,5-Benzenetetracarboxylic acid (labeled as BA) as sensitizer has been bonded to the surface of the nanoparticles, which can sensitize the emission of RE^{3+} in the LaF_3 nanoparticles. The BA- $\text{LaF}_3:\text{RE}^{3+}$ (RE = Eu or Tb) nanoparticles have a broad absorption band in the UV domain, and show enhanced luminescence of RE^{3+} based on an energy transfer from BA ligands to RE^{3+} ions (i.e. the so-called “antenna effect”). Due to the dual protection of organic ligands (BA) and inorganic matrices (LaF_3), BA- $\text{LaF}_3:\text{RE}^{3+}$ (RE = Eu or Tb) nanoparticles have longer excited state lifetimes than $\text{LaF}_3:\text{RE}^{3+}$ (RE = Eu or Tb) nanoparticles as well as lanthanide coordination polymers of BA.

Article titled, “Multifunctional inorganic-organic hybrid nanospheres for rapid and selective luminescence detection of TNT in mixed nitro aromatics via magnetic separation.” by Ma Y et. al in *Talanta*. 2013 Nov 15;116:535-40 reports rapid, sensitive and selective detection of 2,4,6-trinitrotoluene (TNT) in aqueous solution differentiating from other nitroaromatics and independent of complicated instruments is in high demand for public safety and environmental monitoring. In this work, via a simple and versatile method, $\text{LaF}_3:\text{Ce}(3+)-\text{Tb}(3+)$ and Fe_3O_4 nanoparticle-codoped multifunctional nanospheres were prepared through self-assembly of the building blocks. The luminescence of these nanocomposites was dramatically quenched via adding nitroaromatics into the aqueous solution. After the magnetic separation, however, the interference of other nitroaromatics including 2,4,6-trinitrophenol (TNP), 2,4-dinitrotoluene (DNT), and nitrobenzene (NB) was effectively overcome due to the removal of these coexisting nitroaromatics from the surface of nanocomposites. Due to the formation of $\text{TNT}(-)-\text{RCONH}_3(+)$, the TNT was attached to the surface of the nanocomposites and was quantitatively detected by the post exposure luminescence quenching. Meanwhile, the luminescence intensity is negatively proportional to the concentration of TNT in the range of 0.01-5.0 $\mu\text{g}/\text{mL}$ with the 3σ limit of detection (LOD) of 10.2 ng/mL.

Article titled, “Energy transfer from benzoic acid to lanthanide ions in benzoic acid-functionalized lanthanide-doped CaF_2 nanoparticles” by Jianshe Wang et. al in *Applied Surface Science*, Volume 257, Issue 16, 1 June 2011, Pages 7145–7149 reports the preparation of benzoic acid-functionalized $\text{CaF}_2:\text{Ln}^{3+}$ (Ln = Eu or Tb) nanoparticles and their sensitized luminescence. First, to achieve sufficient proof for energy transfer from benzoic acid (BA) to lanthanide ions doped in nanoparticles, we employ Eu^{3+} as the microscopic probe and investigate the luminescent spectra of benzoic acid-functionalized $\text{CaF}_2:\text{Eu}^{3+}$ (BA- $\text{CaF}_2:\text{Eu}^{3+}$) nanoparticles. Next, to further reveal the difference between sensitized luminescence and common luminescence for Eu^{3+} doped in CaF_2 nanoparticles, we study the emission spectra of BA- $\text{CaF}_2:\text{Eu}^{3+}$ nanoparticles excited at 286 nm and 397 nm, respectively. Finally, we analyze and compare the luminescent spectra of BA- $\text{CaF}_2:\text{Tb}^{3+}$ and $\text{CaF}_2:\text{Ce}^{3+}$, Tb^{3+} nanoparticles in detail.

Article titled, "Inkjet printing lanthanide doped nanorods test paper for visual assays of nitroaromatic explosives" by Liang Hong in *Analytica Chimica Acta*, Volume 802, 13 November 2013, Pages 89–94 reports the inkjet printed polyethylenimine (PEI)-coated Ce, Tb co-doped NaGdF₄ nanorods (NaGdF₄:Ce/Tb NRs) onto common filter paper to construct test paper for visual and instant
5 detections of a typical explosive 2,4,6-trinitrophenol (TNP). Polyethylenimine molecules not only facilitate the formation of uniform NaGdF₄ nanorods but also provide specific recognized sites for TNP by the acid–base pairing interaction. The resultant TNP bound at the surface of PEI-coated NaGdF₄:Ce/Tb NRs can strongly quench the phosphorescence with a remarkably high quenching constant by the charge transfer mechanism from NaGdF₄:Ce/Tb NRs to TNP. By printing of the
10 probe on a piece of filter paper, trace amounts of TNP can be visually detected by the appearance of a dark color against a bright green background under a UV lamp. This test paper can detect TNP as low as 0.45 ng mm⁻² by the naked eye, which provides a potential application in the rapid, on-line detections of explosives.

Article titled, "Ligand-centered near-infrared luminescence from lanthanide complexes with
15 chelating nitronyl nitroxide free radicals" by Christophe Lescop in *Inorganic Chemistry*, 09/2000; 39(17), 3740-1 reports Lanthanum(III), europium(III), and gadolinium(III) complexes with chelating nitronyl nitroxide free radicals showing luminescence between 700 and 1000 nm.

Article titled, "Formation and Luminescence Phenomena of LaF₃:Ce³⁺ Nanoparticles and Lanthanide–Organic Compounds in Dimethyl Sulfoxide" by Wei Chen et. al in *The Journal of
20 Physical Chemistry C*, 12/2009; 114(2) reports LaF₃:Ce³⁺-doped nanoparticles synthesis at different temperatures in dimethyl sulfoxide (DMSO) by the chemical reaction of lanthanum nitrate hydrate and cerium nitrate hexahydrate with ammonium fluoride. The formation of Ce³⁺-doped LaF₃ nanoparticles is confirmed by X-ray diffraction and high-resolution transmission electron microscopy. An intense emission at around 310 nm from the d–f transition of Ce³⁺ was observed
25 from the LaF₃:Ce³⁺ powder samples. However, in solution samples, the ultraviolet emission from Ce³⁺ is mostly absent, but intense luminescence is observed in the visible range from blue to red.

Article titled, "Lanthanide-doped calcium phosphate nanoparticles with high internal crystallinity and with a shell of DNA as fluorescent probes in cell experiments" by Sussette Padilla Mondéjar et. al in
30 *J. Mater. Chem.*, 2007, 17, 4153-4159 reports Calcium phosphate nanoparticles prepared by precipitation and stabilized as colloids by coating with DNA. They were doped with europium or terbium during this precipitation (about 2.5 wt%) and showed good fluorescence in the visible part of the spectrum.

Article titled "Lanthanide Sensitization in II–VI Semiconductor Materials: A Case Study with Terbium(III) and Europium(III) in Zinc Sulfide Nanoparticles" by Prasun Mukherjee et. al in
35 *J. Phys. Chem. A*, 2011, 115 (16), pp 4031–4041 reports the sensitization of luminescent lanthanide Tb³⁺ and Eu³⁺ cations by the electronic structure of zinc sulfide (ZnS) semiconductor nanoparticles. Excitation spectra collected while monitoring the lanthanide emission bands reveal that the ZnS

nanoparticles act as an antenna for the sensitization of Tb^{3+} and Eu^{3+} . This model implies that the mechanisms of luminescence sensitization of Tb^{3+} and Eu^{3+} in ZnS nanoparticles are different; namely, Tb^{3+} acts as a hole trap, whereas Eu^{3+} acts as an electron trap. Further testing of this model is made by extending the studies from ZnS nanoparticles to other II–VI semiconductor materials; namely, CdSe, CdS, and ZnSe.

Article titled, “X-ray luminescence of $LaF_3:Tb^{3+}$ and $LaF_3:Ce^{3+}$, Tb^{3+} water-soluble nanoparticles” by Yuanfang Liu in *J. Appl. Phys.* 103, 063105 (2008) reports x-ray luminescence from $LaF_3:Ce^{3+}, Tb^{3+}$ and $LaF_3:Tb^{3+}$ water-soluble nanoparticles. The x-ray luminescence is dominated by emission from Tb^{3+} ions, similar to photo luminescence spectra of the nanoparticle aqueous solutions and spectra from nanoparticle powders precipitated from the aqueous samples. Coating the nanoparticles with an insulating inorganic LaF_3 or organic $H_2N-(CH_2)_{10}-COOH$ layer can enhance the x-ray luminescence from the aqueous nanoparticles.

Article titled, “ $LaPO_4:Ce,Tb$ and $YVO_4:Eu$ nanophosphors: Luminescence studies in the vacuum ultraviolet spectral range” by V. Pankratov in *JOURNAL OF APPLIED PHYSICS*, 110, 053522 (2011) reports comparative analysis of the luminescent properties of nanocrystalline $LaPO_4:Ce, Tb$ and $YVO_4:Eu$ luminescent materials with macrocrystalline analogues, commercially produced by Philips, has been performed under excitation by pulsed vacuum ultraviolet (VUV) synchrotron radiation, ranging from 3.7-40 eV. Special attention was paid to VUV spectral range, which is not reachable with commonly used lamp and laser sources.

US 2012/0288949 A1 relates to a method for determining the presence or amount of a compound in a sample by interparticle distance-dependent sensing, comprising:

(a) contacting the sample suspected of containing the compound with rare earth doped metal oxide nanoparticles; and

(b) detecting the compound by determining the change in luminescent properties of the rare earth doped metal oxide nanoparticles upon contact with the sample.

Article titled, “Trace Explosives Detection by Photoluminescence” by E. Roland Menzel in *The Scientific World JOURNAL* (2004) 4, 55–66 reports a general lanthanide-based photoluminescence approach which shows promise and the ability to photoluminescence-detect trace explosives in the presence of intense background color and/or background fluorescence by time-resolved imaging.

CN 102071027 A discloses water-soluble rare-earth terbium ion-doped cerium fluoride nanocrystallines and a preparation method thereof.

CN 101864298 A discloses a two rare earth complexes doping $Ag @ SiO_2$ fluorescent nanoparticles, characterized in that the fluorescent nanoparticles to double rare earth complexes $Eu^{3+} / Tb^{3+} -PABA-DTPA-APTMS$ silver doped core, the core surface is covered with mesh silica-like structure, with an active surface in Guangxi dioxide amino groups, which double rare earth complexes $Eu^{3+} / Tb^{3+} -PABA-DTPA-APTMS$ mass ratio of silver is: 1:0.176 to 0.2; kernel dioxide silicon mass ratio: 1:5 to 12, and each mg containing 595 ~ 630nmol nanoparticle group.

Article titled, "A Strategy to Protect and Sensitize Near-Infrared Luminescent Nd^{3+} and Yb^{3+} : Organic Tropolonate Ligands for the Sensitization of Ln^{3+} -Doped NaYF_4 Nanocrystals" by Stéphane Petoud in J. Am. Chem. Soc., 2007, 129 (48), pp 14834–14835 reports a strategy to sensitize and protect near-infrared (NIR) emitting Nd^{3+} and Yb^{3+} .

5 The reported prior arts have drawbacks like costly process, high detection level and multi-step method. Therefore it is the need to develop an easier, quick and effective method for detection of nitro containing compounds preferably explosives with low detection level.

OBJECTIVE OF THE INVENTION

10 The main object of the present invention is to provide para amino benzoic acid (pABA) sensitized terbium (Tb^{3+}) doped spherical LaF_3 nanoparticles.

 Another object of the present invention is to provide a method for the detection of highly explosive nitro compounds and determination of pH of a solution utilizing the pABA sensitized terbium (Tb^{3+}) doped spherical LaF_3 nanoparticles.

15 Yet another object of the present invention is to provide pABA functionalized nanoparticles with remarkable enhancement in the luminescence intensity.

 Yet another object of the present invention is to provide a method for the detection of selected nitro compound in the range of 0.04-10 ppm.

20 Yet another object of the present invention is to provide a method for the detection of explosives.

SUMMARY OF THE INVENTION

 Accordingly, the present invention provides a para amino benzoic acid (pABA) sensitized terbium (Tb^{3+}) doped spherical LaF_3 nanoparticles comprising pABA in the ratio of 1:1.

25 In another embodiment, present invention provides a process for preparation of para amino benzoic acid (pABA) sensitized terbium (Tb^{3+}) doped spherical LaF_3 nanoparticles and the said process comprising the steps of:

- 30 i. mixing of lanthanum nitrate hexahydrate ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) and terbium nitrate pentahydrate ($\text{Tb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$) in the ratio ranging between 2 to 10 wt.%;
- ii. adding citric acid solution to the solution as obtained in step (i) at temperature in the range of 60-70°C; followed by adding NH_4F to obtain the reaction mixture;
- iii. refluxing the reaction mixture at temperature in the range of 100 to 110°C for period in the range of 100 to 120 minutes followed by cooling and drying at temperature in the range of 24-30°C to obtain nanoparticles;
- 35 iv. functionalizing the nanoparticles as obtained in step (iii) by dispersing in water followed by adding p-aminobenzoic acid solution at temperature in the range of 60 to 65 °C and refluxing

for period in the range of 100 to 120 minutes at temperature in the range of 70 to 75 °C to obtain surface-functionalized nanoparticles.

In still another embodiment of the present invention, said nanoparticles are useful for detection of nitro group containing compounds by determining the quenching of fluorescence of terbium (Tb^{3+}) doped spherical LaF_3 nanoparticles by the addition nitro group containing compound.

In still another embodiment of the present invention, the detection level of nitro compounds is in the range of 0.04 to 10 ppm.

In yet another embodiment of present invention, the nitro group containing compound is selected from aromatic or aliphatic compounds.

In still another embodiment of present invention, the nitro group containing compounds are selected from nitrobenzene(NB), o-nitrophenol(2-NP), o-nitrotoluene(2-NT), 2,4-dinitrotoluene (2,4-DNT), 2,6-dinitrotoluene (2,6-DNT), 2,4-dinitrophenol(2,4-DNP), picric acid(PA) and 2,4,6-trinitrotoluene (TNT), nitromethane (NM), 1,2,4-butanetriol nitrate (BTTN), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), and 1,3,3-Trinitroazetidine(TNAZ).

In yet another embodiment of present invention, the order of fluorescence quenching is 2,6-dinitrotoluene (2,6-DNT) > o-nitrophenol(2-NP) > 2,4-dinitrophenol(2,4-DNP) > nitrobenzene(NB), 2,4,6-trinitrotoluene (TNT) > picric acid(PA) > 1,3,5-trinitroperhydro-1,3,5-triazine (RDX) > 2,6-dinitrotoluene (2,6-DNT) >> o-nitrotoluene(2-NT) > 1,3,3-Trinitroazetidine(TNAZ) > octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) > nitromethane (NM), 1,2,4-butanetriol nitrate (BTTN) and the values of quenching constant (k_Q), obtained for TNT, PA, 2-NP, 2,4-DNT, 2,4-DNP are 12295, 5738, 1683, 3296, 2103M⁻¹ respectively.

In yet another embodiment of present invention, the pABA functionalized terbium (Tb^{3+}) doped spherical LaF_3 nanoparticles shows 100 -120 times enhancement in the luminescence intensity in comparison to direct excitation of Tb^{3+} ion.

In still another embodiment of the present invention, said nanoparticles are useful for the detection of pH acidic or alkaline solution and the said nano particles possess UV-absorption peak at 265 at pH=3.

In still another embodiment of the present invention, the life time value of the surface functionalized nanoparticles in absence of an analyte is 0.1177 ns.

In still another embodiment of the present invention, the life time value of the surface functionalized nanoparticles in presence of picric acid analyte is the concentration of 18, 61.25 and 125 ppm are 0.1158, 0.0883, and 0.0806 ns respectively.

ABBREVIATIONS

Nitrobenzene (NB), o-nitrophenol(2-NP), o-nitrotoluene(2-NT), 2,4-dinitrotoluene (2,4-DNT), 2,6-dinitrotoluene (2,6-DNT), 2,4-dinitrophenol (2,4-DNP), picric acid (PA), 2,4,6-trinitrotoluene (TNT) and some aliphatic nitro compounds such as nitromethane (NM), 1,2,4-

butanetriol nitrate (BTTN), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), and 1,3,3-Trinitroazetidine(TNAZ).

BRIEF DESCRIPTION OF THE DRAWINGS

5 **Figure 1** depicts XRD (X-ray diffraction) and IR spectra of $\text{LaF}_3:\text{Tb}^{3+}$ nanoparticles with and without pABA along with the JCPDS Card No. 82-0690.

Figure 2 depicts the morphology of $\text{LaF}_3:\text{Tb}^{3+}@$ pABA nanoparticles (a-c) along with (d) its SAED (Selected Area Electron Diffraction) and (e) its EDAX (Energy Dispersive X-ray Analysis) spectra. Rod shape morphology of higher dopant concentration is also shown (f).

10 **Figure 3** depicts (a) Absorption, (b) excitation and (c) emission spectra of $\text{LaF}_3:\text{Tb}^{3+}$ with and without pABA along with (d) schematic diagram for the energy transfer in $\text{LaF}_3:\text{Tb}^{3+}@$ pABA nanoparticles. Excitation and emission wavelength are fixed at 265 and 546 nm, respectively

Figure 4 depicts Effect of pH on the emission spectra $\text{LaF}_3:\text{Tb}^{3+}@$ pABA nanoparticles at $\lambda_{\text{ex}} = 265$ nm. Inset shows the integrated area under the curve for 546 nm peak.

15 **Figure 5** depicts Emission spectra of $\text{LaF}_3:\text{Tb}^{3+}@$ pABA nanoparticles at $\lambda_{\text{ex}} = 265$ nm with the change in concentration of (a) PA and (b) TNT. Inset shows their respective Stern-Volmer plots.

Figure 6 depicts Emission spectra of $\text{LaF}_3:\text{Tb}^{3+}@$ pABA nanoparticles at $\lambda_{\text{ex}} = 265$ nm with the change in concentration of (a) NP, (b) DNP and (c) DNT. Inset shows their respective Stern-Volmer plots.

20 **Figure 7** depicts Bar graph showing the quenching efficiencies (%) for all the analyzed analyte at their fixed concentration of 0.1 mM.

Figure 8 depicts overlap of emission spectrum spectrum of pABA with with UV spectra for (a) NP, 2,4-DNP, PA, DNT and (b) 2,6-DNT, TNT, RDX.

25 **Figure 9** depicts Histogram showing the particle size distribution (DLS (Dynamic Light Scattering) measurement) of $\text{LaF}_3:\text{Tb}^{3+}@$ pABA nanoparticles

Figure 10 depicts Absorption spectra of of $\text{LaF}_3:\text{Tb}^{3+}@$ pABA nanoparticles at different pH.

Figure 11 depicts Emission spectra of $\text{LaF}_3:\text{Tb}^{3+}@$ pABA nanoparticles at different concentration of Tb^{3+} ions.

30 **Figure 12** depicts Emission spectra of $\text{LaF}_3:\text{Tb}^{3+}@$ pABA nanoparticles at $\lambda_{\text{ex}} = 265$ nm with the change in concentration of TNT (ppb level). Inset shows their respective Stern-Volmer plots.

Figure 13 depicts Energy level diagram of all the selected nitro compounds.

Figure 14 depicts Decay profile for $\text{LaF}_3:\text{Tb}^{3+}@$ pABA nanoparticles at varying concentration of (a) PA and (b) TNT.

35 **Figure 15** depicts colour change of the particles in presence of explosives under UV light irradiation.

DETAILED DESCRIPTION OF THE INVENTION

The present invention provide para amino benzoic acid (pABA) sensitized terbium (Tb^{3+}) doped spherical LaF_3 nanoparticles and a method for the detection of highly explosive nitro compounds and determination of pH of a solution utilizing the para amino benzoic acid (pABA) sensitized terbium (Tb^{3+}) doped spherical LaF_3 nanoparticles.

The present invention provides a process for the detection of nitro group containing compound using the terbium (Tb^{3+}) doped spherical LaF_3 nanoparticles comprising of the steps of:

- a) determining the fluorescence of terbium (Tb^{3+}) doped spherical LaF_3 nanoparticles;
- 10 b) adding para amino benzoic acid (pABA) to terbium (Tb^{3+}) doped spherical LaF_3 nanoparticles of step (a) in the ratio ranging between 2 to 10 wt.% and determining the enhanced fluorescence; and
- c) adding the sample of step (b) with the nitro group containing compound and determining the quenching of fluorescence of terbium (Tb^{3+}) doped spherical LaF_3 nanoparticles by nitro group containing compound.

The present invention provides a process wherein the nitro group containing compound is selected from aromatic or aliphatic compounds.

20 The present invention provides a method for the detection of pH of an unknown acidic or alkaline solution by studying the variation of the photoluminescence properties of the para amino benzoic acid (pABA) sensitized $LaF_3:Tb^{3+}$ nanomaterials at different pH.

25 The present invention provides para amino benzoic acid (pABA) functionalized $LaF_3:Tb^{3+}$ nanoparticles (Figure 3a) with strong broad UV-absorption peak having maximum at 265 nm having absorption intensity highest at pH=3.

The pABA functionalized nanoparticles show remarkable (>100 times) enhancement in the luminescence intensity as compared to direct excitation of Tb^{3+} ion as shown in Figure 3c.

30 The detection level for the selected nitro compound is in the range of 0.04-10 ppm. The surfaced functionalised nanomaterials is able to detect TNT upto 50 ppb.

The technique of utilizing the Tb^{3+} doped NPs sensitized by para amino benzoic acid (pABA) have potential application in the detection of explosives.

35 The present invention provides Tb^{3+} doped nanoparticles which are highly sensitive as well as selective to the aromatic nitro compounds as compared with the aliphatic nitro compounds.

The present invention provides detection of nitro group containing compounds selected from the group consisting of nitrobenzene(NB), o-nitrophenol(2-NP), o-nitrotoluene(2-NT), 2,4-dinitrotoluene (2,4-DNT), 2,6-dinitrotoluene (2,6-DNT), 2,4-dinitrophenol(2,4-DNP), picric acid(PA) and 2,4,6-trinitrotoluene (TNT), nitromethane (NM), 1,2,4-butanetriol nitrate (BTTN),
5 octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), and 1,3,3-Trinitroazetidine(TNAZ).

The present invention provides the order of fluorescence quenching as follows: 2,6-dinitrotoluene (2,6-DNT) > o-nitrophenol(2-NP) > 2,4-dinitrophenol(2,4-DNP) > nitrobenzene(NB), 2,4,6-trinitrotoluene (TNT) > picric acid(PA) > 1,3,5-trinitroperhydro-1,3,5-triazine (RDX) > 2,6-dinitrotoluene (2,6-DNT) >> o-nitrotoluene(2-NT) > 1,3,3-Trinitroazetidine(TNAZ) > octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) > nitromethane (NM), 1,2,4-butanetriol nitrate (BTTN).
10 (Figure 8 and 13)

The present invention provides the values of quenching constant (k_Q), obtained using above Stern-Volmer equation for TNT, PA, 2-NP, 2,4-DNT, 2,4-DNP which are as follows 12295, 5738, 1683, 3296, 2103M⁻¹.
15

Life time value of the surface functionalized nanoparticles in absence of any analyte is 0.1177 ns. Further, in presence of 18, 61.25 and 125 ppm picric acid analyte life time values of the surface functionalized nanoparticles are 0.1158, 0.0883, and 0.0806 ns (nanosecond) respectively.
20

Life time values of the surface functionalized nanoparticles in presence of 10, 20 and 60 ppm TNT analyte are 0.0790, 0.0889, and 0.0785 ns respectively. (Refer Fig: 14)

25 EXAMPLES

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

Reagents and Materials

Lanthanum nitrate hexahydrate (La(NO₃)₃.6H₂O) (99.99%), terbium nitrate pentahydrate (Tb(NO₃)₃.5H₂O) (99.9%), Ammonium fluoride (NH₄F) (99.99%) were purchased from Aldrich. Anhydrous citric acid (99.5%) and dimethyl sulfoxide (99.9%) were purchased from Merck. p-aminobenzoic acid from SDFCL and picric acid (PA) obtained from Aldrich. All the others nitro compounds listed below are obtained from DRDO-HEMRL, Pune. Deionised water was used to make aqueous solutions. All the materials were used as received.
30
35

Example 1**Synthesis of LaF₃:Tb³⁺spheres**

Tb_xLa_{1-x}F₃ (where x=0.02, 0.04, 0.06, 0.08 and 0.1) nanoparticles were synthesized.

3 g of anhydrous citric was dissolved in 20 ml of water in 250 ml RB (Round bottom) flask. 60 ml of
5 DMSO (Dimethyl sulphoxide) and 1 ml conc. NH₄OH were added to the citric acid solution to adjust
the pH to 5 and stirred nicely. About 2 mmol (depending upon doping conc.) of lanthanum nitrate
hexahydrate (La(NO₃)₃.6H₂O) and stoichiometric amount of terbium nitrate pentahydrate
(Tb(NO₃)₃.5H₂O) were dissolved in 2 ml water. This lanthanide solution was added drop wise to the
10 citric acid solution at 70°C temperature. A dense white turbidity appeared. White dense turbidity
converted to a pale white suspension when 3ml aq. solution of 7 mmol NH₄F was added slowly. The
reaction mixture was refluxed at 110°C temperature under water circulation for two hours and then
cooled to 30 °C. The nanoparticles were collected by centrifugation, washed with deionized (DI)
water and methanol, and dried at 30 °C.

15 Surface-functionalization of nanoparticles

0.2 g of the resulting nanoparticles was dispersed in 50 ml water and formed a colloidal
solution. 0.2 g of p-aminobenzoic acid was dissolved in 30 ml NaOH solution. This p-aminobenzoic
acid solution was added slowly to the nanoparticles colloid at 65 °C and refluxed for two hours at 75
°C. The surface-functionalized nanoparticles were separated by centrifugation, washed twice with
20 water and methanol and dried at 30 °C.

Example 2**Preparation of analyte solution**

500 mg picric acid was dissolved in 1000 ml water to prepare a stock solution of 500ppm
25 (2.18mM) strength. This mother solution was followed by a two-fold serial dilution to prepare the
solutions of 250, 125, 62.5, 31, 15.5, 8, 4, 2 ppm concentrations. These analyte solutions were mixed
with equal volume of aqueous dispersion of the nanoparticles and analyzed, i.e the analyte
concentrations in the experimental solutions were again diluted to half concentration.

Example 3

30 3 mg of 2,4,6-trinitrotoluene was dissolved in 25 ml water to prepare a 120 ppm (0.52mM)
stock solution. This solution was diluted with water to prepare 100ppm, 80ppm, 60ppm, 40ppm,
20ppm solutions which on mixing with equal volume dispersion of nanoparticles gave the
experimental solutions.

Example 4

35 7 mg of nitrophenol was dissolved in 250 ml of water to prepare a 0.2 mM stock solution (28
ppm) This solution was diluted with water to prepare 14 ppm, 7 ppm, 3.5 ppm, 1.75 ppm solution

which on mixing on mixing with equal volume dispersion of nanoparticles gave the experimental solutions.

Example 5

9 mg of 2,4-dinitrophenol was dissolved in 250 ml of water to prepared a 0.2 mM stock solution (36 ppm) This solution was diluted with water to prepare 18 ppm, 9 ppm, 4.5 ppm, 2 ppm solution which on mixing with equal volume dispersion of nanoparticles gave the experimental solutions.

Example 6

9 mg of 2,4-dinitrotoluene was dissolved in 250 ml of water to prepared a 0.2 mM stock solution (36 ppm) This solution was diluted with water to prepare 18 ppm, 9 ppm, 4.5 ppm, 2 ppm solution which on mixing with equal volume dispersion of nanoparticles gave the experimental solutions.

Example 7

6.9 mg of o-nitrotoluene was dissolved in 250 ml water to prepare a 0.2mM stock solution.

Example 8

9 mg of nitrobenzene was dissolved in 250 ml water to prepare a 0.2mM stock solution.

Example 9

9 mg of nitromethane was dissolved in 250 ml water to prepare a 0.2mM stock solution.

Example 10

12 mg of 1,2,4-butanetriol nitrate was dissolved in 250 ml water to prepare a 0.2mM stock solution.

Example: 11

9.6 mg of 1,3,3-Trinitroazetidide was dissolved in 250 ml water to prepare a 0.2mM stock solution.

Example 12

11 mg of RDX was dissolved in 250 ml water to prepare a 0.2mM stock solution.

Example 13

15 mg of octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine was dissolved in 250 ml water to prepare a 0.2mM stock solution.

30

Characterization**1. XRD study**

All the samples analyzed (before and after surface functionalization) had clear resemblance with the tysonite structure of LaF_3 (JCPDS card 82-0690) as shown in Figure: 1(a-c).

The average crystallite size of the nanoparticles were calculated using Scherrer equation ($d = k\lambda/\beta\cos\theta$), where λ is the X-ray wavelength (0.154 nm), β is the full width at half-maximum (fwhm) of a diffraction peak, θ is the diffraction angle, k is a constant (0.89). Average crystallite size of $\text{LaF}_3:\text{Tb}^{3+}$

and $\text{LaF}_3:\text{Tb}^{3+}$ @pABA nanoparticles are in the range of (5.52 - 6.29) and (4.50 - 5.53) nm respectively, at different concentration of the dopant, Tb^{3+} as summarized in Table 1.

There is a broadening of peaks after the surface functionalization as can be observed from the gradual increase in the FWHM value of the (111) plane from (2.49 - 2.71) to (2.70 - 3.12) nm on moving from $\text{LaF}_3:\text{Tb}^{3+}$ to $\text{LaF}_3:\text{Tb}^{3+}$ @PABA nanoparticles (Table 1).

The reason for the shrinking phenomenon of the unit cell volume is due to the smaller ionic radius of Tb^{3+} (0.923 Å) as compared to that of La^{3+} ion (1.032 Å). All the above analysis indicates that Tb^{3+} ions have been successfully doped into the lattice of LaF_3 nanomaterials.

Table 1: Crystallite size, Lattice parameter, Unit cell volume and FWHM (Full Width Half Maximum) of pABA functionalised and non-functionalised $\text{LaF}_3:\text{Tb}^{3+}$ NPs.

S.No.	Sample	Crystallite size (nm)	Lattice parameter		Unit cell volume (Å ³)	FWHM (111)
			a=b	c		
1	$\text{LaF}_3:\text{Tb}^{3+}$ (2%)	5.52	7.19	7.43	332.90	2.70
2	$\text{LaF}_3:\text{Tb}^{3+}$ (4%)	5.90	7.17	7.44	331.99	2.50
3	$\text{LaF}_3:\text{Tb}^{3+}$ (6%)	5.74	7.17	7.50	334.10	2.61
4	$\text{LaF}_3:\text{Tb}^{3+}$ (8%)	5.59	7.17	7.42	330.95	2.71
5	$\text{LaF}_3:\text{Tb}^{3+}$ (10%)	6.29	7.16	7.31	325.23	2.49
6	$\text{LaF}_3:\text{Tb}^{3+}$ (2%)@PABA	4.50	7.19	7.43	340.67	3.12
7	$\text{LaF}_3:\text{Tb}^{3+}$ (4%)@PABA	5.28	7.17	7.44	336.10	2.70
8	$\text{LaF}_3:\text{Tb}^{3+}$ (6%)@PABA	5.08	7.17	7.50	341.27	2.93
9	$\text{LaF}_3:\text{Tb}^{3+}$ (8%)@PABA	4.57	7.17	7.42	338.62	3.02
10	$\text{LaF}_3:\text{Tb}^{3+}$ (10%)@PABA	5.53	7.16	7.31	332.71	3.14

2. IR study

The broad peak (Figure 1d) in the range of 3000 - 3500 cm^{-1} can be assigned to the stretching vibration of O-H group of carboxylic acid. Peaks at 1583 cm^{-1} and 1410 cm^{-1} are assigned to asymmetric and symmetric stretching vibrations of carboxylic group. Strong peak at 1016 cm^{-1} is due to C-O stretching of citric acid. The spectra of the functionalized nanoparticle (Figure 1e) show two new peaks at 1497 cm^{-1} and 747 cm^{-1} which is due to C-C stretching vibration and out of plane C-H bending vibrations of benzene ring, respectively. The peaks at 1558 cm^{-1} and 1400 cm^{-1} are due to the carboxylic acid group of pABA. Broad peak above 3000 cm^{-1} can be assigned to amine group of pABA. The above analysis confirms that pABA has been successfully attached on the surface of the nanoparticles.

3. Morphology and elemental composition analysis

Figure 2(a-c) shows the HRTEM (High Resolution Transmission Electron Microscope) images of as prepared surface functionalized $\text{LaF}_3:\text{Tb}^{3+}@\text{pABA}$ NPs which shows the morphology of spherical shape. The average size of the spherical nanoparticles is 5.2 nm which is in good agreement with the value calculated from XRD. The lattice fringes are clearly observed and the experimentally observed d-spacing is found to be 0.32 nm which coincides with the (111) plane of tysonite structure (JCPDS card 82-0690) of LaF_3 . Crystalline nature of the nanoparticles is well understood from the SAED pattern (Figure 2d) and the major diffraction has been assigned to their corresponding planes. Figure 2e shows the EDAX spectra of as-prepared $\text{LaF}_3:\text{Tb}^{3+}@\text{pABA}$ NPs. All the typical peaks corresponding to La, F, Tb are observed in the spectra. At higher dopant concentration (10 at% of Tb^{3+}), the spherical shape morphology of the nanoparticles get converted to a rod shape morphology with an average length ~10 nm and width of ~2 nm as shown in Figure 2f.

The particles are found to be agglomerated in nature. Figure 9 shows the histogram of particle size distribution from the DLS measurement. The individual particles are found to be agglomerated in the size range of ~120-170 nm with ~150 nm constituting half of the total populations.

4. Absorption study

The absorption spectra of pABA functionalized and non-functionalized $\text{LaF}_3:\text{Tb}^{3+}$ nanoparticles is shown in Figure 3a. In case of functionalized nanoparticles a new strong broad absorption peak having maximum at 265 nm appears which is not present for as prepared non-functionalized $\text{LaF}_3:\text{Tb}^{3+}$ nanoparticles. The functionalized nanoparticles show lowest absorption intensity at pH=1 (Figure 10). Absorption intensity is highest at pH=3 which is almost double as compared to the absorption intensity at pH=7. The above analysis further confirms that the pABA sensitized $\text{LaF}_3:\text{Tb}^{3+}$ shows highest absorption activity at pH=3 and subsequently all the photoluminescence analysis has been performed at this optimum pH. Very low UV absorption in the alkaline medium where free $-\text{NH}_2$ group is present is due to very little dispersibility of the nanoparticles at pH=13.

5. Photoluminescence studies

All the photoluminescence studies were performed in aqueous medium. Taking 50 mg/250 ml aqueous (pH=3) dispersions of pABA functionalized and non-functionalized $\text{LaF}_3:\text{Tb}^{3+}$ samples to examine the energy transfer or sensitization of Tb^{3+} by pABA (Figure 3b). When the functionalised nanoparticles are excited at pABA absorption maximum at 265 nm, it gives ~100 times stronger luminescence as compared to direct excitation (360 nm) of Tb^{3+} ion as shown in Figure 3c. The energy transfer process can be explained through the schematic diagram in Figure 3d.

Radiative transitions of Tb^{3+} ions gives typical three characteristic strong emission bands centered at 490 nm, 546 nm and 586 nm, among which the peak at 546 nm is the strongest one.

Sensitized luminescence intensity increases with increase in Tb^{3+} ion concentration in the LaF_3 nanoparticles (Figure 11). But at 10% Tb^{3+} concentration luminescence reduces due to concentration quenching. In the present study, the optimum concentration of the Tb^{3+} ion was found to be 8%.

5 Example: 14

Variation on the photoluminescence properties with change of pH:

A 1000 ml of 0.2M HCl solution was prepared by diluting 17 ml conc. HCl solution to 1000ml. This solution was followed by ten fold serial dilution to prepare HCl solutions of strength 0.02, 0.002, 0.0002, 0.00002 and 0.000002(M).

10 Equal volume of 50mg in 250 ml water dispersion of $LaF_3:Tb^{3+}(8\%)$ @ pABA nanoparticles were mixed with the acid solution to prepare the experimental solutions of pH 1, 2, 3, 4, 5, 6. 0.4g of NaOH was dissolved in 50ml water to prepare a 0.2 (M) solution. And following the above procedure experimental solutions of pH 13, 12, 11, 10, 9 and 8 were prepared. All the samples were excited at 265 nm and variation in luminescence intensity of these samples were recorded in the
15 wavelength range of 450-700 nm (Figure 4).

Luminescence intensities in the pH range of 4-7 are almost same as shown in Figure 4a. The integrated area of 546 nm peak shows that maximum at pH=3 (Figure 4a). After pH=7, a slight enhancement in the luminescence is observed till pH=9. In the strong alkaline medium (pH=10-13), luminescence reduces below the neutral medium luminescence (Figure 4b). Very low luminescence
20 intensity in strongly acidic medium (pH=1) and strongly alkaline medium (pH=13) is experimentally supported by very low UV absorption intensities at that pH values (Figure 10). Surface area to volume ratio ($4\pi r^2/4\pi r^3/3$) of these very small nanoparticles (~5 nm) is around 10^7 cm^{-1} . A plot of integrated area of the most intense peaks at 546 nm vs pH shows a straight line having negative slope and taking an intercept on y-axis (Inset of Figure 4b). This linear relationship can be used to detect
25 pH of unknown alkaline medium.

Detection of nitro explosives

All the experiment for the detection of the nitro compounds (Example 15-26) were performed at the pH = 3 and $Tb^{3+} = 8\%$ ions concentration. Energy of LUMO of most of the aliphatic nitro
30 explosives lies above that of pABA and hence no electron transfer as well as luminescence quenching is observed by the aliphatic nitro explosives (Figure 13).

Example 15

To the aqueous dispersion of the pABA sensitized $LaF_3:Tb^{3+}$ nanoparticles, aqueous solution of nitrobenzene (NB), was added and its photoluminescence property was studied.

35 Example 16

To the aqueous dispersion of the pABA sensitized $LaF_3:Tb^{3+}$ nanoparticles, aqueous solution of o-nitrophenol (2-NP), was added and its photoluminescence property was studied.

Photoluminescence spectra (Figure 6) of $\text{LaF}_3:\text{Tb}^{3+}@\text{pABA}$ in NP show that this nitro compound can quench the luminescence at very low concentrations of the analyte (2 ppm or $12.5\mu\text{M}$). Calculated values of quenching constant (k_Q), obtained for 2-NP is 1683M^{-1} (Figure 7).

Example 17

5 To the aqueous dispersion of the pABA sensitized $\text{LaF}_3:\text{Tb}^{3+}$ nanoparticles, aqueous solution of o-nitrotoluene(2-NT) was added and its photoluminescence property was studied.

Example 18

To the aqueous dispersion of the pABA sensitized $\text{LaF}_3:\text{Tb}^{3+}$ nanoparticles, aqueous solution of 2,4-dinitrotoluene (2,4-DNT) was added and its photoluminescence property was studied.
10 Photoluminescence spectra (Figure 6) of $\text{LaF}_3:\text{Tb}^{3+}@\text{pABA}$ in 2,4-DNT show that this nitro compounds can quench the luminescence at very low concentrations of the analyte (2 ppm or $12.5\mu\text{M}$). Calculated values of quenching constant (k_Q), obtained for 2,4-DNT is 3296M^{-1} (Figure 7).

Example 19

To the aqueous dispersion of the pABA sensitized $\text{LaF}_3:\text{Tb}^{3+}$ nanoparticles, aqueous solution
15 of 2,6-dinitrotoluene (2,6-DNT) was added and its photoluminescence property was studied.

Example 20

To the aqueous dispersion of the pABA sensitized $\text{LaF}_3:\text{Tb}^{3+}$ nanoparticles, aqueous solution of 2,4-dinitrophenol(2,4-DNP) was added and its photoluminescence property was studied.
20 Photoluminescence spectra (Figure 6) of $\text{LaF}_3:\text{Tb}^{3+}@\text{pABA}$ in 2,4-DNP show that this nitro compounds can quench the luminescence at very low concentrations of the analyte (2 ppm or $12.5\mu\text{M}$). Calculated values of quenching constant (k_Q), obtained for 2,4-DNP is 2103M^{-1} (Figure 7).

Example 21

To the aqueous dispersion of the pABA sensitized $\text{LaF}_3:\text{Tb}^{3+}$ nanoparticles, aqueous solution of picric acid (PA) was added and its photoluminescence property was studied. Luminescence
25 quenching is observed at very low concentrations of picric acid (2.25 ppm or $10\mu\text{M}$) (Fig: 5). Calculated values of quenching constant (k_Q), obtained for PA is 5738M^{-1} (Figure 7).

Example 22

To the aqueous dispersion of the pABA sensitized $\text{LaF}_3:\text{Tb}^{3+}$ nanoparticles, aqueous solution of 2,4,6-trinitrotoluene (TNT) was added and its photoluminescence property was studied.
30 Luminescence quenching is observed at very low concentrations of TNT (10 ppm or $50\mu\text{M}$) (Fig: 5). Calculated values of quenching constant (k_Q), obtained for TNT is 12295M^{-1} (Figure 7).

Example 23

To the aqueous dispersion of the pABA sensitized $\text{LaF}_3:\text{Tb}^{3+}$ nanoparticles, aqueous solution of nitromethane (NM) was added and its photoluminescence property was studied.

Example 24

To the aqueous dispersion of the pABA sensitized $\text{LaF}_3:\text{Tb}^{3+}$ nanoparticles, aqueous solution of 1,2,4-butanetriol nitrate (BTTN) was added and its photoluminescence property was studied.

Example 25

To the aqueous dispersion of the pABA sensitized LaF₃:Tb³⁺ nanoparticles, aqueous solution of octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) was added and its photoluminescence property was studied.

5 Example 26

To the aqueous dispersion of the pABA sensitized LaF₃:Tb³⁺ nanoparticles, aqueous solution of 1,3,3-Trinitroazetidene(TNAZ) was added and its photoluminescence property was studied.

Figure 5 shows the photoluminescence spectra of LaF₃:Tb³⁺@pABA in picric acid and T.N.T solution. Luminescence quenching is observed at very low concentrations of TNT (10 ppm or 50μM) and picric acid (2.25 ppm or 10μM). Photoluminescence spectra (Figure 6) of LaF₃:Tb³⁺@pABA in NP, 2,4-DNP and 2,4-DNT show that these nitro compounds can also quench the luminescence at very low concentrations of the analyte (2 ppm or 12.5μM).

Figure 12 shows very sensitive detection of TNT at ppb level. At such low concentration the luminescence intensity change at ⁵D₄- ⁷F₄ is more clearly seen than for ⁵D₄- ⁷F₅ transition. The luminescence at 490nm was used for Stern-Volmer plot. The surfaced functionalised nanomaterials were able to detect TNT upto 50 ppb.

Calculated values of quenching constant (k_Q), obtained using above Stern-Volmer equation for TNT, PA, 2-NP, 2,4-DNT, 2,4-DNP are 12295, 5738, 1683, 3296, 2103M⁻¹ respectively. Among the above analysed nitrocompounds, TNT has remarkably high quenching constant. A comparison of quenching efficiency of the all the selected nitrocompounds at a particular concentration (0.1mM) is shown in the bar-graph of Figure 7. It shows negligible quenching by aliphatic nitro explosives except for RDX (explained below). Thus the nanoparticles are highly sensitive as well as selective to the aromatic nitro compounds as compared with the aliphatic nitro compounds.

The order of quenching for the above analysed nitrocompounds was; 2,6-dinitrotoluene (2,6-DNT) > o-nitrophenol(2-NP) > 2,4-dinitrophenol(2,4-DNP) > nitrobenzene(NB), 2,4,6-trinitrotoluene (TNT) > picric acid(PA) > 1,3,5-trinitroperhydro-1,3,5-triazine (RDX) > 2,6-dinitrotoluene (2,6-DNT) >> o-nitrotoluene(2-NT) > 1,3,3-Trinitroazetidene(TNAZ) > octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) > nitromethane (NM), 1,2,4-butanetriol nitrate (BTTN). (Figure 8 and 13) UV-absorption study as shown in the Figure 8 reveals that emission spectra of pABA overlaps effectively with the UV absorption spectra of 2,4-DNT, 2-NP, 2,4-DNP and picric acid. This can explain high quenching performance of 2,4-DNT, 2-NP and 2,4-DNP. There is a very less overlap for 2,6-DNT, TNT and RDX. So the quenching mechanism for 2,6-DNT and TNT is mainly electron transfer mechanism. This observation can also explain very low quenching performance by 2,6-DNT and RDX. Hence, pABA sensitised LaF₃:Tb³⁺ NPs can be potential materials for using as a sensor for the detection of highly explosive nitrocompounds.

Example 27**Lifetime measurements**

Life time of the nanoparticles were studied in presence and absence of the analytes (PA and TNT) and were recorded by fixing the excitation and emission wavelengths at 265 nm and 546 nm respectively as shown in Figure 14. Life time of the surface functionalized nanoparticles in absence of any analyte is 0.1177 ns. In presence of 18, 61.25 and 125 ppm picric acid life time values are 0.1158, 0.0883, and 0.0806 ns respectively. Life time values for 10, 20 and 60 ppm TNT are 0.0790, 0.0889, and 0.0785 ns respectively. (Fig: 15)

10 ADVANTAGES OF INVENTION

1. High detection level.
2. Method can detect nitro containing explosives.
3. It can be used for determining the pH of a solution.
4. Process of synthesis of Tb^{3+} doped LaF_3 is simple and quick.

15

20

25

30

35

Claim

1. Para amino benzoic acid (pABA) sensitized terbium (Tb^{3+}) doped spherical LaF_3 nanoparticles comprising pABA in the ratio of 1:1.
- 5 2. A process for preparation of para amino benzoic acid (pABA) sensitized terbium (Tb^{3+}) doped spherical LaF_3 nanoparticles and the said process comprising the steps of:
 - i. mixing of lanthanum nitrate hexahydrate ($La(NO_3)_3 \cdot 6H_2O$) and terbium nitrate pentahydrate ($Tb(NO_3)_3 \cdot 5H_2O$) in the ratio ranging between 2 to 10 wt.%;
 - 10 ii. adding citric acid solution to the solution as obtained in step (i) at temperature in the range of 60-70°C; followed by adding NH_4F to obtain the reaction mixture;
 - iii. refluxing the reaction mixture at temperature in the range of 100 to 110°C for period in the range of 100 to 120 minutes followed by cooling and drying at temperature in the range of 24-30°C to obtain nanoparticles;
 - 15 iv. functionalizing the nanoparticles as obtained in step (iii) by dispersing in water followed by adding p-aminobenzoic acid solution at temperature in the range of 60 to 65 °C and refluxing for period in the range of 100 to 120 minutes at temperature in the range of 70 to 75 °C to obtain surface-functionalized nanoparticles.
- 20 3. The nanoparticles as claimed in claim 1, wherein the said nanoparticles are useful for detection of nitro group containing compounds by determining the quenching of fluorescence of terbium (Tb^{3+}) doped spherical LaF_3 nanoparticles by the addition nitro group containing compound.
- 25 4. The nanoparticles as claimed in claim 1, wherein the detection level of the nitro compounds in the range of 0.04 to 10 ppm.
5. The method as claimed in claim 3, wherein the nitro group containing compound is selected from aromatic or aliphatic compounds.
- 30 6. The method as claimed in claim 3, wherein the nitro group containing compounds are selected from nitrobenzene(NB), o-nitrophenol(2-NP), o-nitrotoluene(2-NT), 2,4-dinitrotoluene (2,4-DNT), 2,6-dinitrotoluene (2,6-DNT), 2,4-dinitrophenol(2,4-DNP), picric acid(PA) and 2,4,6-trinitrotoluene (TNT), nitromethane (NM), 1,2,4-butanetriol

nitrate (BTTN), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), and 1,3,3-Trinitroazetidene(TNAZ).

7. The method as claimed in claim 3, wherein the order of fluorescence quenching is 2,6-dinitrotoluene (2,6-DNT) > o-nitrophenol(2-NP) > 2,4-dinitrophenol(2,4-DNP) > nitrobenzene(NB), 2,4,6-trinitrotoluene (TNT) > picric acid(PA) > 1,3,5-trinitroperhydro-1,3,5-triazine (RDX) > 2,6-dinitrotoluene (2,6-DNT) >> o-nitrotoluene(2-NT) > 1,3,3-Trinitroazetidene(TNAZ) > octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) > nitromethane (NM), 1,2,4-butanetriol nitrate (BTTN) and the values of quenching constant (k_Q), obtained for TNT, PA, 2-NP, 2,4-DNT, 2,4-DNP are 12295, 5738, 1683, 3296, 2103M⁻¹ respectively.
8. The method as claimed in claim 3, wherein the pABA functionalized terbium (Tb³⁺) doped spherical LaF₃ nanoparticles shows 100 -120 times enhancement in the luminescence intensity in comparison to direct excitation of Tb³⁺ion.
9. The doped, sensitized spherical nanoparticles as claimed in claim 1, wherein said nanoparticles are used for detection of pH acidic or alkaline solution and the said nano particles possess UV-absorption peak at 265 at pH=3.
10. The terbium (Tb³⁺) doped spherical LaF₃ nanoparticles as claimed in claim 1, wherein the life time value of the surface functionalized nanoparticles in absence of an analyte is 0.1177 ns and in presence of picric acid analyte in the concentration of 18, 61.25 and 125 ppm are 0.1158, 0.0883, and 0.0806 ns respectively.

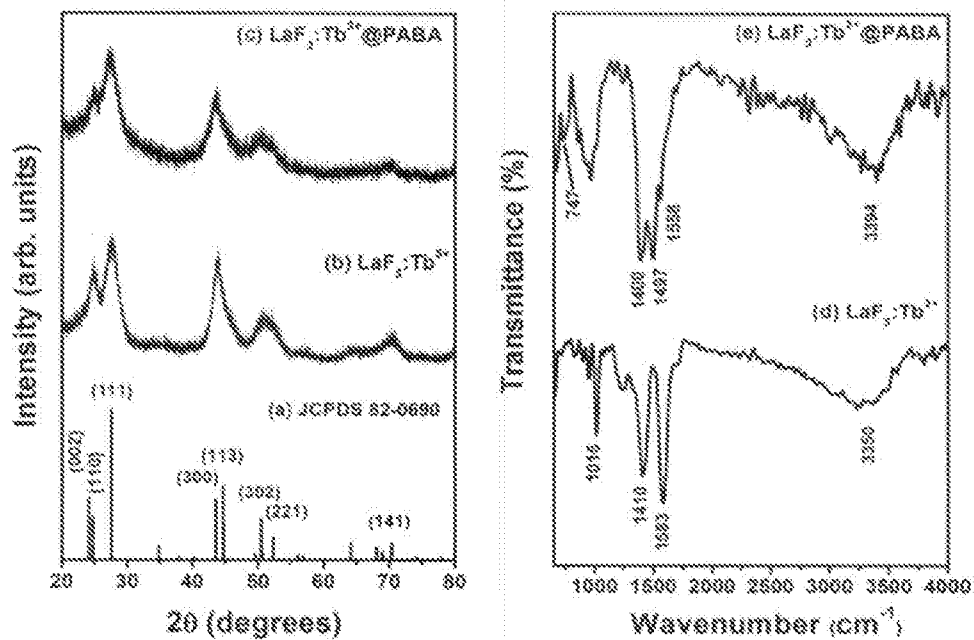


Figure 1

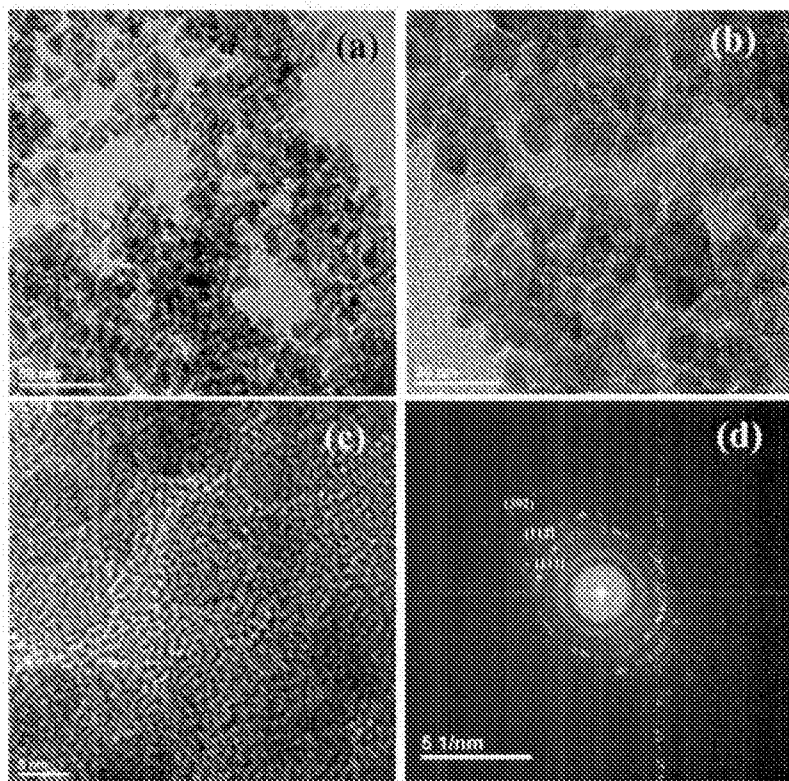


Figure 2

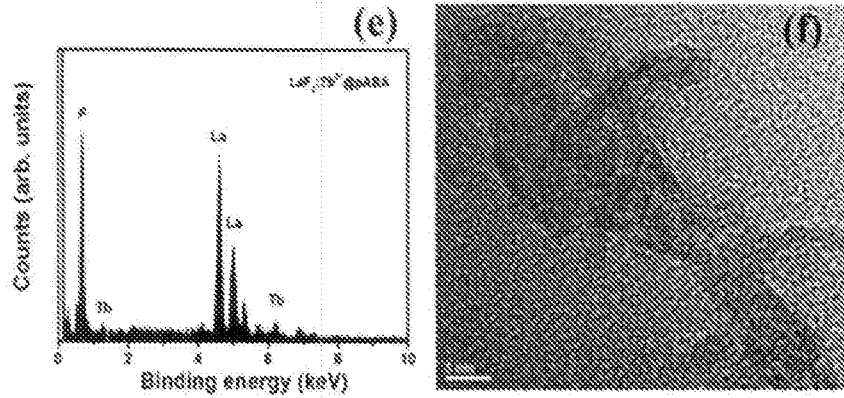


Figure 2

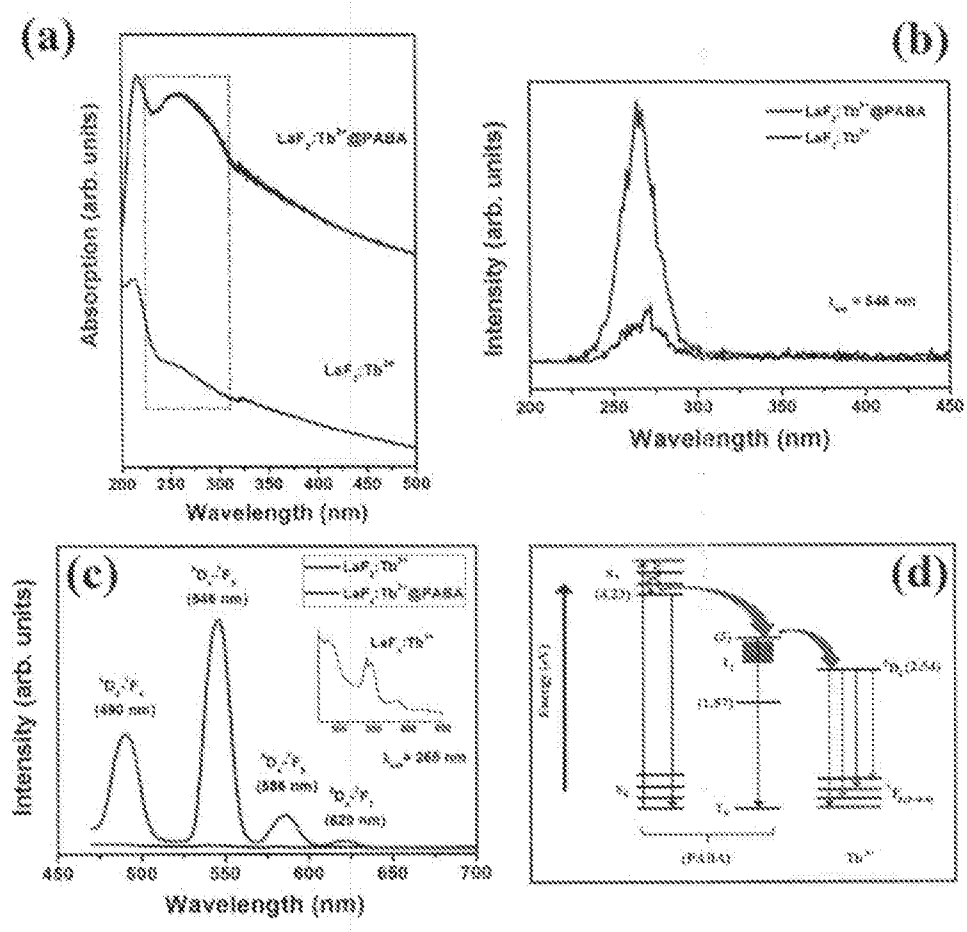


Figure 3

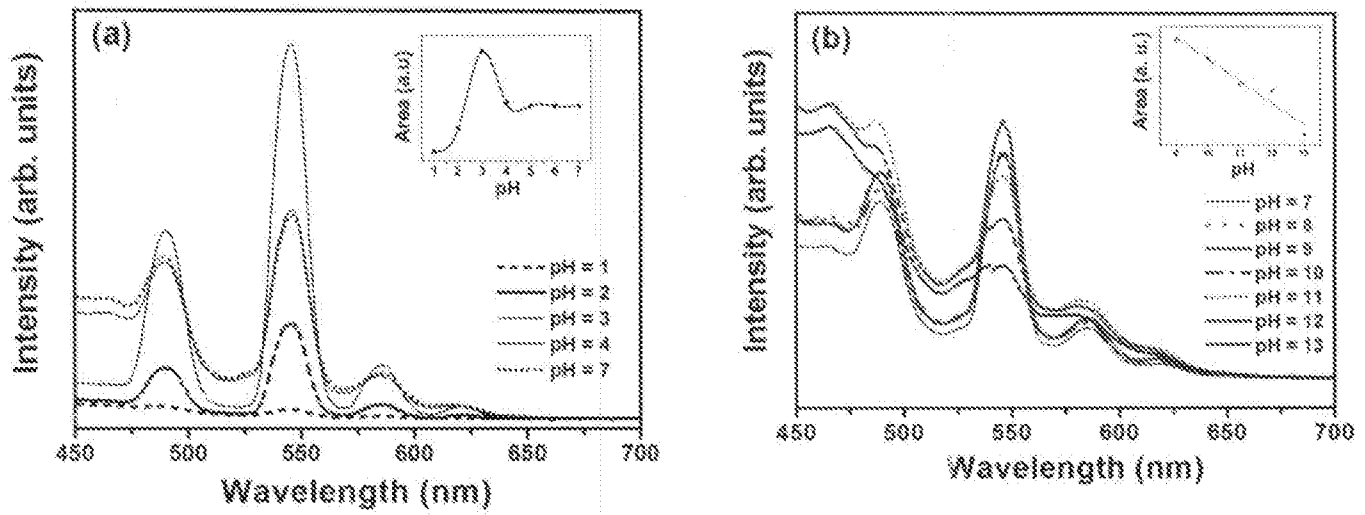


Figure 4

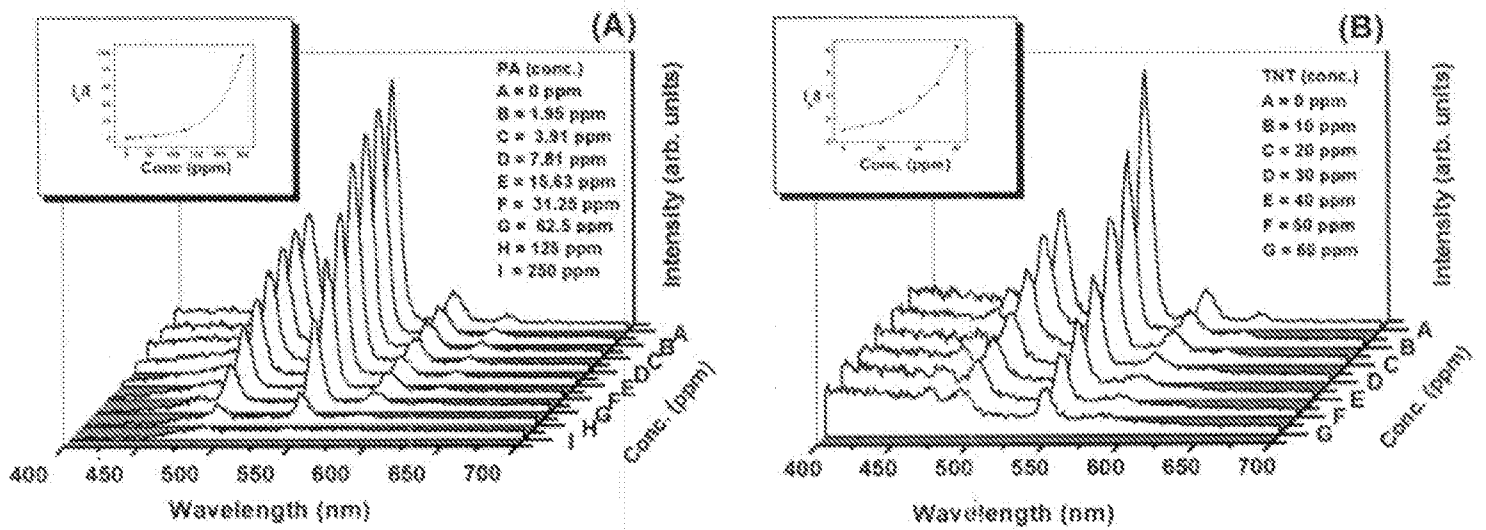


Figure 5

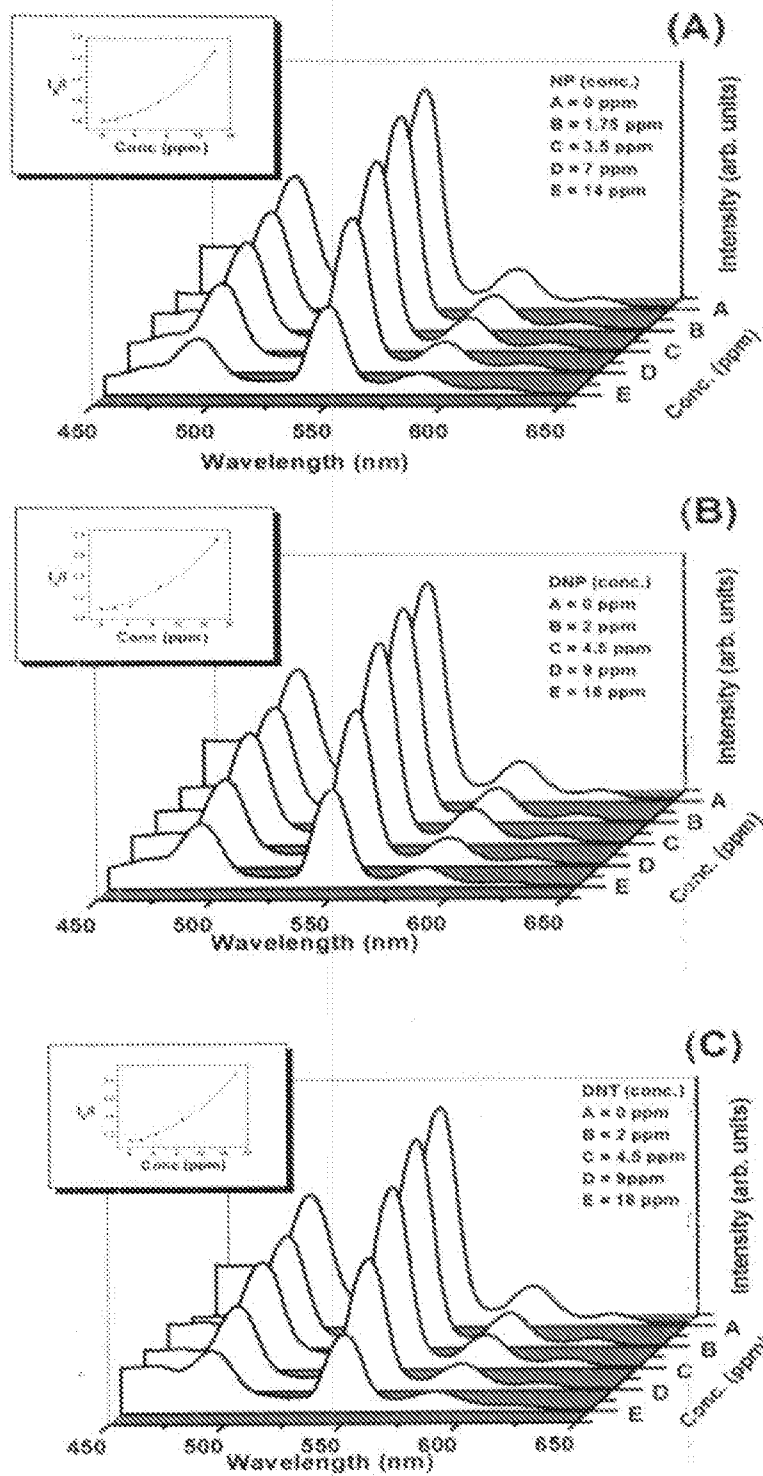


Figure 6

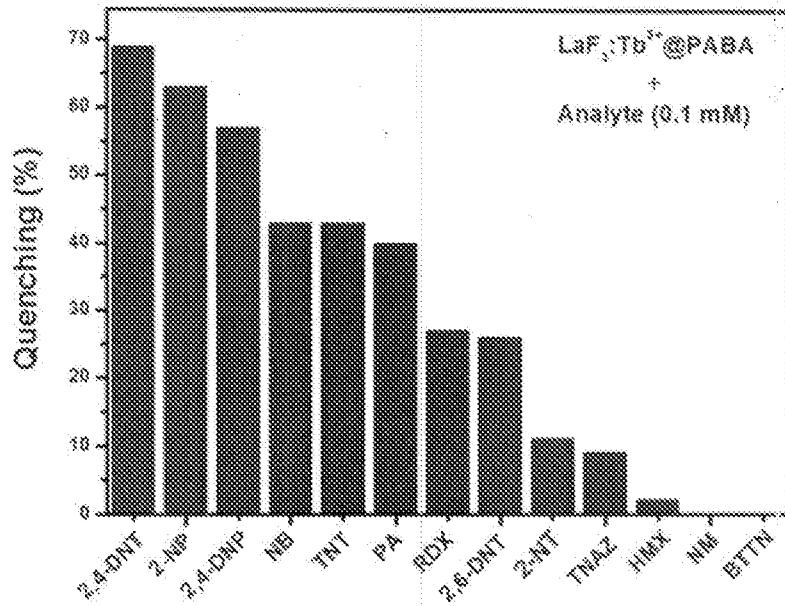


Figure 7

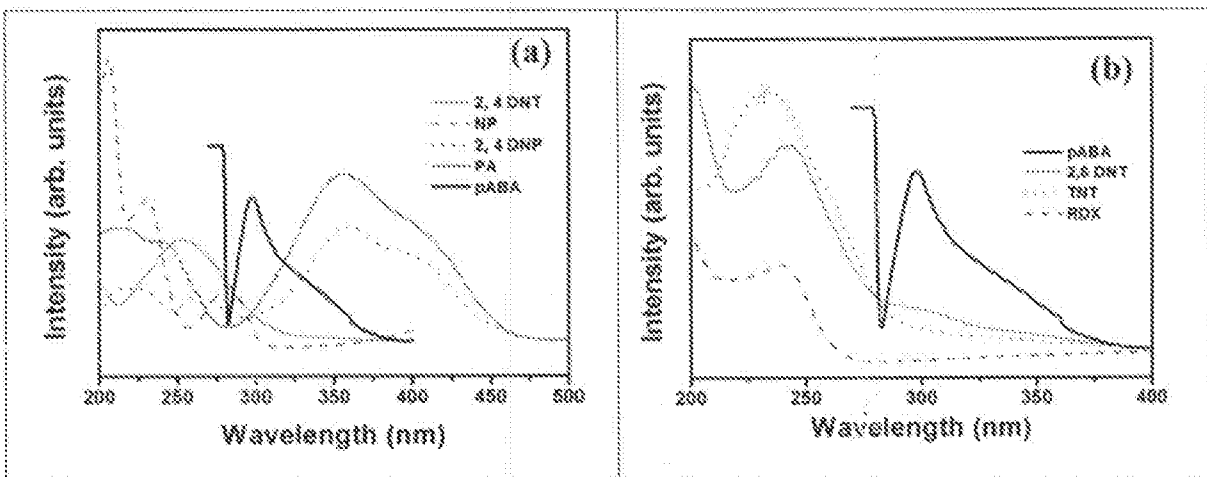


Figure 8

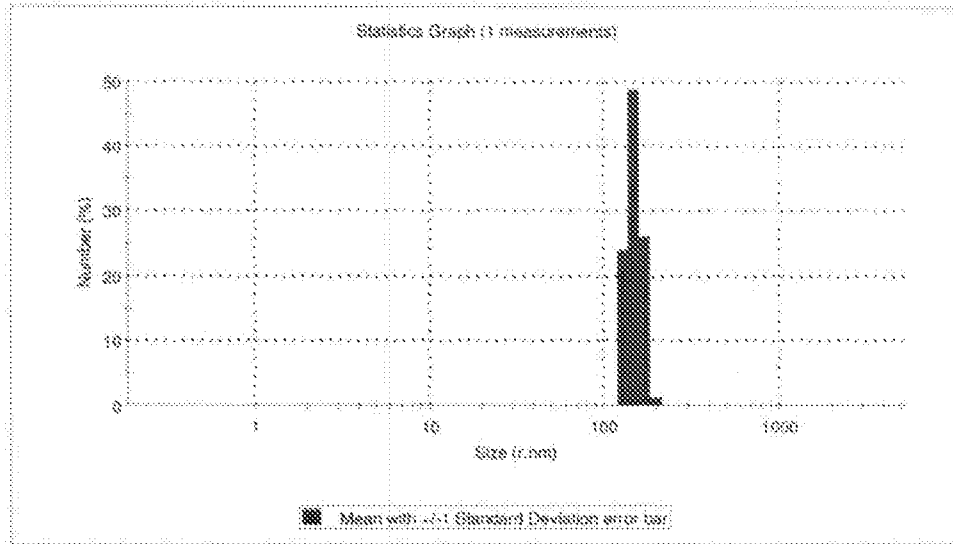


Figure 9

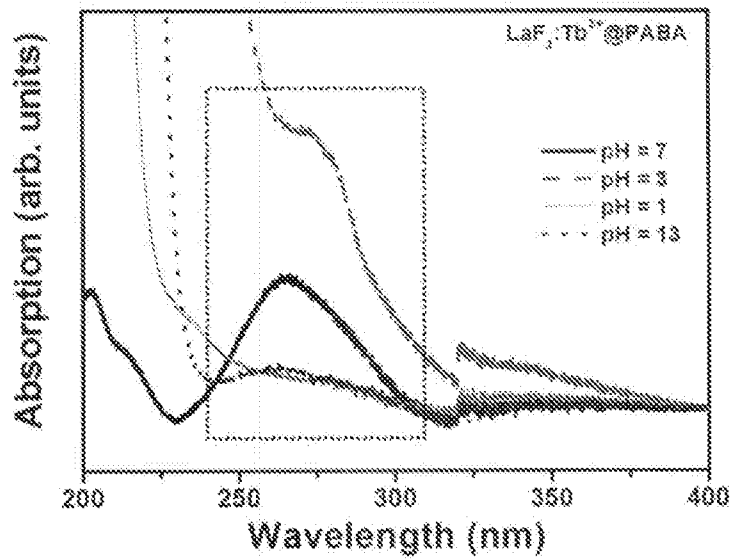


Figure 10

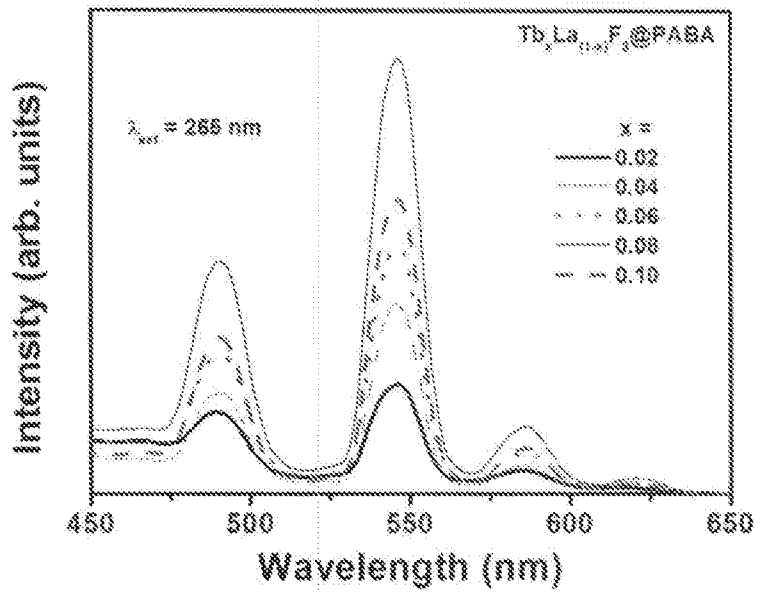


Figure 11

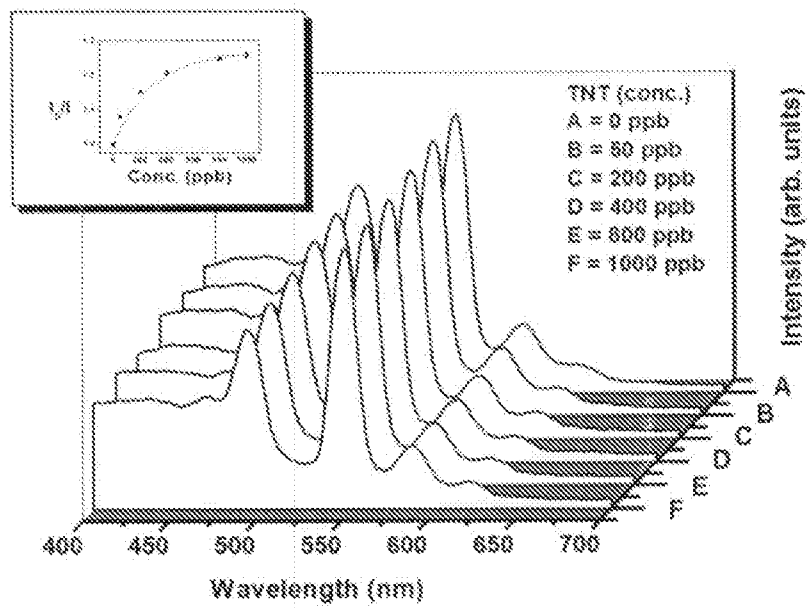


Figure 12

8/9

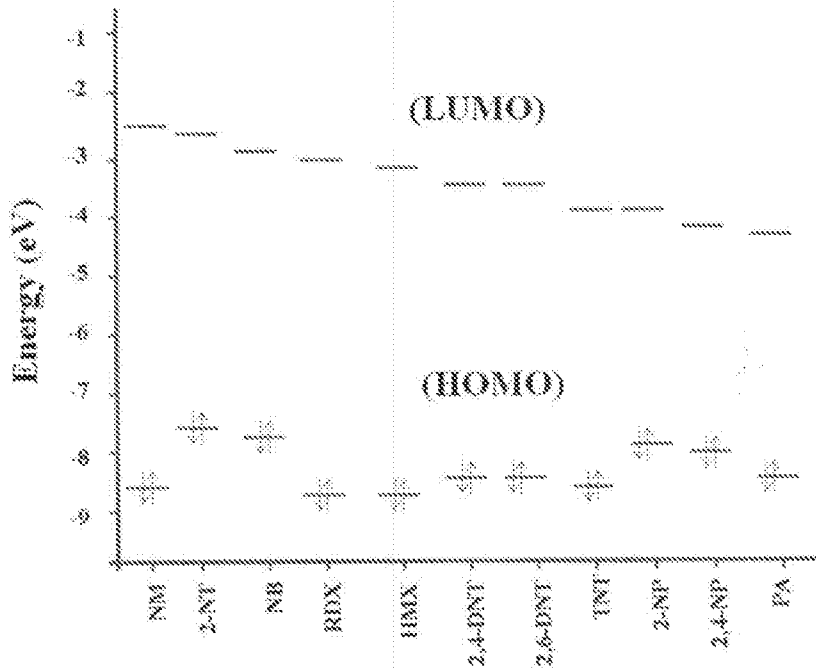


Figure 13

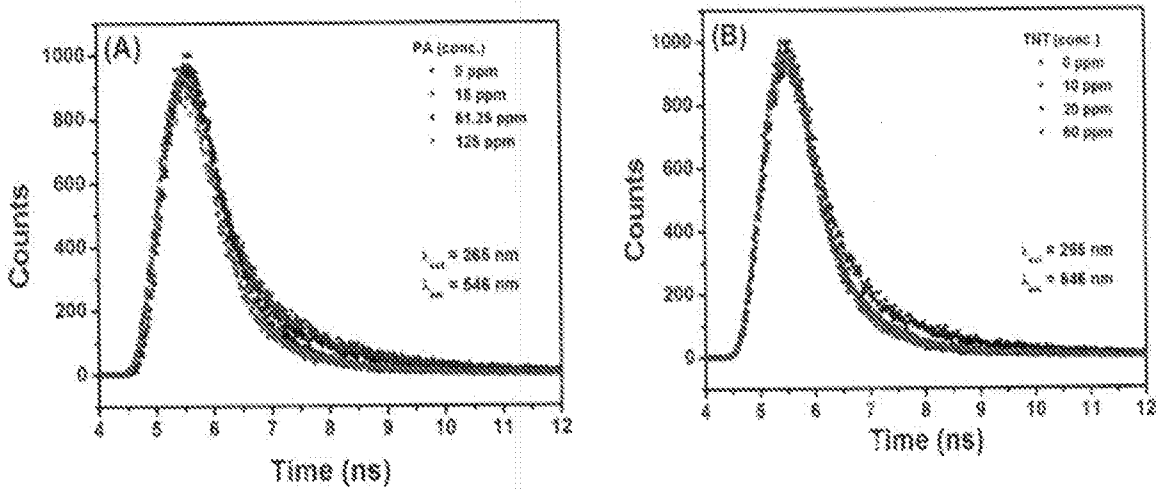


Figure 14

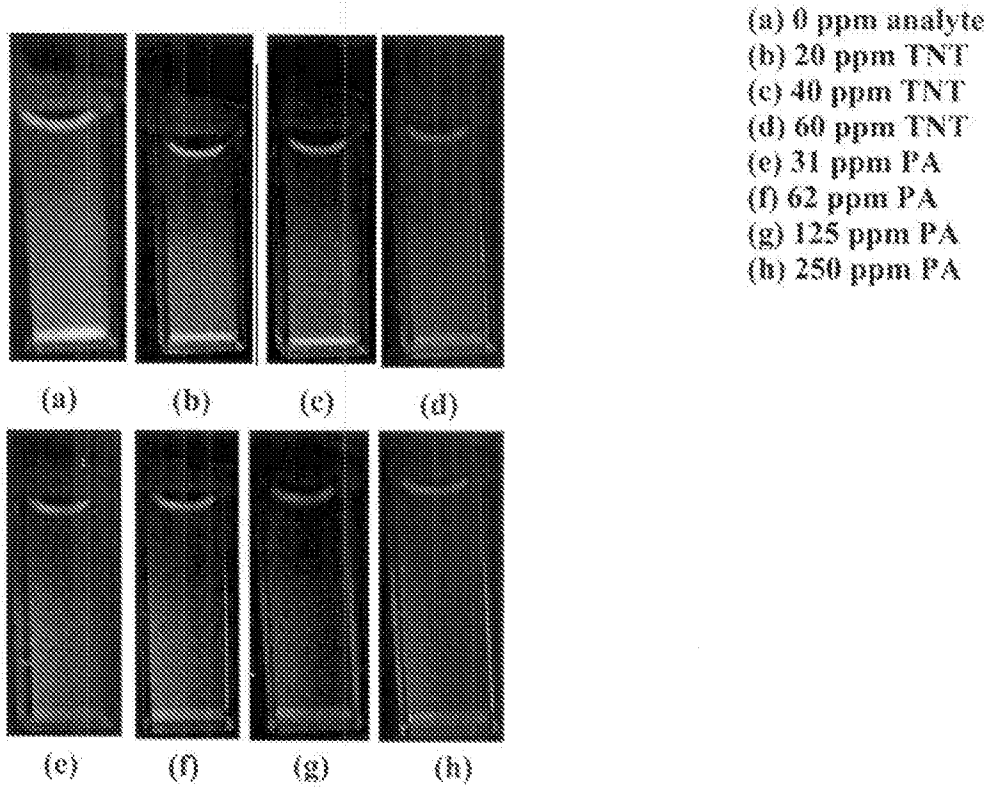


Fig: 15

INTERNATIONAL SEARCH REPORT

International application No
PCT/IN2015/050082

A. CLASSIFICATION OF SUBJECT MATTER
INV. G01N21/64 B82Y15/00
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)
G01N B82Y
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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	DEBASISH GHOSH ET AL: "p-Aminobenzoic acid (pABA) sensitization of LaF 3 :Tb 3+ nanoparticles and its applications in the detection of explosive materials", RSC ADVANCES: AN INTERNATIONAL JOURNAL TO FURTHER THE CHEMICAL SCIENCES, vol. 5, no. 14, 7 January 2015 (2015-01-07), pages 10468-10478, XP055234310, GB ISSN: 2046-2069, DOI: 10.1039/C4RA15304A the whole document ----- -/--	1-10

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier application or patent but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "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
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search 8 December 2015	Date of mailing of the international search report 17/12/2015
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Michalitsch, Richard

INTERNATIONAL SEARCH REPORT

International application No
PCT/IN2015/050082

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	SUWEN LI ET AL: "Enhanced emission of ultra-small-sized LaF ₃ :RE ₃₊ (RE = Eu, Tb) nanoparticles through 1,2,4,5-benzenetetracarboxylic acid sensitization", NANOSCALE, vol. 4, no. 18, 1 January 2012 (2012-01-01), page 5619, XP055234359, United Kingdom ISSN: 2040-3364, DOI: 10.1039/c2nr31206a	1,2
Y	abstract Section 2. Experimental table 1	3-10
Y	----- MA YINGXIN ET AL: "Multifunctional inorganic-organic hybrid nanospheres for rapid and selective luminescence detection of TNT in mixed nitroaromatics via magnetic separa", TALANTA, vol. 116, 20 July 2013 (2013-07-20), pages 535-540, XP028743942, ISSN: 0039-9140, DOI: 10.1016/J.TALANTA.2013.07.033 Section: Experimental section, point 2.4; figure 1 page 539; figures 2-6	1-10
Y	----- BARIS KOKUOZ ET AL: "Color Kinetic Nanoparticles", JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, vol. 130, no. 37, 17 September 2008 (2008-09-17), pages 12222-12223, XP055234364, US ISSN: 0002-7863, DOI: 10.1021/ja803898y the whole document	1-10
A	----- Physics of the Solid State From Fizika Tverdogo Tela, 1 January 2005 (2005-01-01), pages 1479-1484, XP055234321, Retrieved from the Internet: URL: http://rd.springer.com/content/pdf/10.1134/1.2014496.pdf [retrieved on 2015-12-08] Section 3. Fluoride nanoparticles in an SG matrix figures 2-4 -----	1-10