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# A luminescent lanthanide complex-based anion sensor with electron-donating methoxy groups for monitoring multiple anions in environmental and biological processes

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### HIGHLIGHTS

- Ternary complex was strong red emissive.
- ► The sensor exhibits striking emission changes to anions.
- Luminescent could display luminescence change for fluoride anion.

### G R A P H I C A L A B S T R A C T

A ternary europium (III) tris(2-thenoyltrifluoroacetonate) with 2-(3,4,5-trimethoxy phenyl)imidazo[4,5-f]-1,10-phenanthroline (1) was prepared and it can detect various anions such as  $F^-$ ,  $ACO^-$  and  $H_2PO_4^-$ . Spectroscopic studies of UV-vis, Fluorescence and NMR present that the sensor exhibits striking emission changes to fluoride (purple), acetate anions (green) and  $H_2PO_4^-$  (blue), respectively. More importantly, transparent hybrid thick films (poly-methyl methacrylate) show intense red emissions and give rise to luminescence change in fluoride anion containing DMSO solution.



0 equiv. 5 equiv. F 5 equiv. H2PO4 5 equiv. Acc

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## ABSTRACT

We designed a ternary europium (III) tris(2-thenoyltrifluoroacetonate) with 2-(3,4,5-trimethoxyphenyl)imidazo[4,5-f]-1,10-phenanthroline (1) ligands for the luminescent detection of various anions, such as fluoride, acetate and dihydrogen phosphate. Characterization of the sensor's photophysical properties and via NMR showed that the sensor exhibits striking emission changes to fluoride (purple), acetate (green) and dihydrogen phosphate (blue) anions, respectively. Its fluorescence lifetime was determined to be 1.10 ms for europium ions and the complex showed an overall quantum yield of 10% in DMSO.

Furthermore, transparent hybrid thick films composed of the europium complex and poly-methyl methacrylate matrix were successfully prepared via copolymerization. The resulting film overall displayed intense red emissions associated with europium ions. Fluorescence microscopic evaluation

\* Corresponding author. Tel.: +86 20 39310258. E-mail address: qmwang@scnu.edu.cn (Q. Wang). Anion Sensor Polymer films Polymethyl methacrylate Fluoride Acetate Dihydrogen phosphate showed a homogenous distribution of aggregates with average diameters of  $30-50 \mu m$  throughout the film. The accordingly produced film could give rise to a luminescence change to purple in response to fluoride anions.

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### Introduction

Since different anions such as fluoride, hydrogen sulfate and acetate are critical components in environment, biological and metabolic processes. The specific structural and reactive receptors composed of organic fluorophores were designed and prepared in monitoring particular anions [1–8].

The trivalent lanthanide ions are well-known for their luminescent properties in the visible (Eu, Tb) and near-infrared region (Yb, Pr, Nd) of the electromagnetic spectrum and long emission lifetime ranging from microseconds (e.g. Yb, Nd) to milliseconds (e.g. Eu and Tb). Thus autofluorescence from the much shorter lived biomolecules (sub-microseconds) can easily be filtered via time-gated techniques and the penetration depth for imaging purposes can be maximized using NIR emitting probes. Unfortunately, trivalent lanthanide ions inherently suffer from weak light absorption capabilities because their f-f transitions are Laporte-forbidden resulting in molar absorption coefficients ( $\varepsilon$ ) smaller than  $10 \text{ Lmol}^{-1} \text{ cm}^{-1}$  for most of the absorption transitions [9]. This is extremely low compared to organic chromophores, which are generally at least 5000 time larger [10]. Thus an obvious solution to this problem is to introduce an organic chromophore that acts as an "antenna" and has the capacity to absorb more light because of its more intense absorption bands to subsequently transfer the excitation energy to the lanthanide ion by intramolecular energy transfer (indirect excitation) [9,11].

Not surprisingly, lanthanide-organic chromophore complexes have caught the attention of many researchers in various disciplines over the past few decades, not in the least because of their extraordinary properties. Their sharp and intense emission bands and versatile color changes are sensitive to external interaction with guest molecules such as anions. Lanthanide complexes are markedly oxophilic and positively charged, thereby providing strong electrostatic interactions with anions [12]. Furthermore, the aforementioned long emission lifetimes, obviation of practical problems associated with autofluorescence and Rayleigh scattering in biological samples make them desirable probes in biological and biomedical research.

A number of groups have previously reported various lanthanide-based luminescent sensors with various sensitivities and specificities. Parker et al. [11], Faulkner et al. [13], and Gunnlaugsson et al. [14] developed multidentate cyclen-based lanthanide complexes for the selective detection of various anions, including bicarbonate. Tsukube's group reported lanthanide complexes of tris(2-pyridylmethyl)amines [15] and a series of N<sub>3</sub>, O-mixed donor chiral tripods that formed stabile lanthanide complexes [16] as anion-responsive luminescent compounds for anions such as chloride and nitrate. Ziessel and co-workers [12] prepared complexes of europium and terbium with bis-[(6'-carboxy-2,2'-bipyridine-6-yl)]phenylphosphine oxide donor ligands for the detection of ADP<sup>3–</sup>, ATP<sup>4–</sup>, and phosphate anions. However, because there are few sensors available that detect multiple anions and, to the best of our knowledge, no sensor that is capable of detecting dihydrogen phosphate anions, we aimed to synthesize a europiumbased sensor that would accomplish this.

In this paper, we describe the two step synthesis, initial characterization, and application of a novel antenna ligand, 2-(3,4,5-trimethoxy-phenyl)imidazo[4,5-f]-1,10-phenanthroline (1) for a europium-based Eu-(TTA)3-1 anion sensor. This novel complex (Fig. 1A) could be applied as an effective receptor and sensor for the luminescent detection of acetate (AcO<sup>-</sup>), fluoride (F<sup>-</sup>) and dihydrogen phosphate  $(H_2PO_4^-)$  anions. Since hybrid materials of polymers and lanthanide complexes display beneficial properties, such as mechanical flexibility and durability, thermal stability, and easy processability, such configurations have attracted much attention, particularly for applications in electronics and optics [17,18]. Because simple embedding of lanthanide ions in the polymer matrix often leads to inhomogeneous distribution of the probe and associated luminescence artifacts [9,19,20]. such as local quenching, we opted to covalently couple the Eu-(TTA)<sub>3</sub>-1 anion sensor monomers via co-polymerization to the polymer host [9,17,21]. We thus managed to introduce the europium-based anion sensor into a polymeric host, poly-methyl methacrylate



**Fig. 1.** Ternary europium complex-based luminescent anion sensor. (A) Molecular structure of Eu(TTA)<sub>3</sub>-1, consisting of the chromophoric antenna 2-(3,4,5-trimeth-oxy-phenyl)imidazo[4,5-f]-1,10-phenanthroline and the ternary europium complex; R: tris(2-thenoyltrifluoroacetonate). (B) Photo visualizing the color change in response to the addition of 5 eq. of different anions (tetrabutyl ammonium salts). Excitation was performed with a portable UV-lamp (254 and 365 nm).

(PMMA), to create transparent polymeric films that were sensitive to fluoride anions and showed homogenous emission signals.

#### Experimental

#### Materials and techniques

Tetrabutyl ammonium fluoride trihydrate (97%), tetrabutyl ammonium chloride (97%), tetrabutyl ammonium bromide (98%), tetrabutyl ammonium iodide (98%), tetrabutyl ammonium hydrogensulfate (97%), tetrabutyl ammonium dihydrogen phosphate (98%), tetrabutyl ammonium acetate (97%) were purchased from Sigma-Aldrich company. Other chemicals and materials were acquired from local commercial suppliers, used as received and were of the highest purity available. <sup>1</sup>H-NMR spectra were recorded at 293 K on a Varian MR 400 MHz NMR spectrometer (Agilent Technologies Ltd., Beijing, China) using tetramethylsilane (TMS) as an internal standard. Visible and luminescence spectra, emission lifetime, and absolute quantum yields were measured on an Agilent 8453 UV-visible spectrophotometer (Agilent Technologies Ltd., Beijing, China) and Edinburgh FLS920 spectro-fluorimeter (Edinburgh Instruments Ltd., Livingston, UK), respectively. The errors for the lifetime measurements were within 10%. Absolute quantum vields  $(\phi)$  were determined at ambient temperature according to Wrighton et al. [22] and further described by Carlos et al. [23] were calculated as  $\phi = A/(R_s - R_H)$ , where A is the area under the complex emission spectrum, and  $R_S$  and  $R_H$  are the diffuse reflectance (fixed wavelengths) of the complex and of the reflecting standard. The deviations in the quantum yields were estimated to be 25% [22]. The luminescence of PMMA films was measured by using a front-surface accessory to clamp the samples. LC-MS was performed on an Agilent 1100 HPLC-MS with an electrospray ionization source. Thermogravimetric analysis (TGA) was carried out on a STA 409 PC system (Netzsch-Gerätebau GmbH, Selb, Germany) under air at a rate of 10 °C/min. Dynamic light scattering was measured with a BI-200SM Laser Light Scattering Goniometer (Brookhaven Instruments Ltd., Redditch, UK). The fluorescence images were taken using a Nikon Eclipse TS100 inverted fluorescence microscope system (Japan), equipped with a 50 W mercury lamp source.

#### Synthesis procedure

Synthesis of 2-(3,4,5-trimethoxy phenyl)imidazo[4,5-f]-1,10phenanthroline (ligand (L)) was essentially performed as described in more detail previously [24]. Briefly, 1,10-Phenanthroline-5,6dione (50 mg, 0.24 mmol) was mixed with ammonium acetate (0.5 g, 6.5 mmol) and subsequently dissolved in 3 ml glacial acetic acid. Under stirring, 3,4,5-trimethoxybenzaldehyde (47 mg, 0.24 mmol) in acetic acid (1.5 ml) was added to the previously prepared mixture. The solution was heated to 90 °C for 2 h and quenched with 50 ml distilled water. An aqueous ammonium solution (30%, 3 ml) was added to neutralize the solution to pH 7. The precipitate was collected and washed with distilled water. The crude product was dried in vacuo overnight. Further purification steps were performed by flash column chromatography with alumina (aluminum oxide 90 deactivated neutral) and CHCl<sub>2</sub>/MeOH (10/1) as elution solvents. The second band was collected as the titled compound (70 mg, 75%) and the product presented itself as a yellow solid. Subsequent NMR and MS analysis showed: <sup>1</sup>H-NMR (DMSO- $d_6$ )  $\delta = 9.05$  (2H, d, J = 4.0 Hz, H<sub>a</sub>), 8.94 (2H, d,  $I = 8.0 \text{ Hz}, H_c$ , 7.86 (2H, m,  $I = 8.0 \text{ Hz}, H_b$ ), 7.62 (2H, s, H<sub>d</sub>), 4.00 (6H, s), 3.76 (3H, s); MS analysis (LCMS) showed that the major product was: *m*/*z* 387.5 (MH<sup>+</sup>).

The preparation of EuTTA<sub>3</sub>·2H<sub>2</sub>O was performed according to the method described by Lenaerts et al. [17]. Synthesis of Eu-TTA<sub>3</sub>-1: Compound 1 (16.6 mg, 0.05 mmol) was dissolved in 10 ml ethanol, to which EuTTA<sub>3</sub>·2H<sub>2</sub>O (40.8 mg, 0.05 mmol) was added. The whole mixture was refluxed for 3 h and allowed to cool to room temperature. The resulting precipitate was collected and washed twice with distilled water to give the titled complex (50 mg, 83%) as a yellow powder. Infrared spectroscopic analysis showed: IR (KBr) v = 3696, 1603, 1535, 1306, 1246, 1180, 1105, 897, 723 cm<sup>-1</sup>. EA found: C, 45.88%; H, 2.31%; N, 4.81%, Anal. Calcd. for C<sub>46</sub>H<sub>30</sub>EuF<sub>9</sub>N<sub>4</sub>O<sub>9</sub>S<sub>3</sub> = EuTTA<sub>3</sub>-1: C, 45.97%; H, 2.52%; N, 4.66%.

EuTTA<sub>3</sub>-1 doped poly-methyl methacrylate (PMMA) thick films were prepared as follows: compound EuTTA<sub>3</sub>-1 was dissolved in MMA monomer (concentration from 0.1 mg to 0.9 mg/5 ml MMA). Azobisisobutyronitrile (AIBN) was used as the radical poly-merization initiator and added to the above mentioned solution to a final concentration of 0.1%. The mixture was heated in an oil-bath at 75 °C for 10 min under stirring. After the monomers became viscous, the pre-polymers were quickly cast onto a glass substrate. Further polymerization was conducted in an oven at 70 °C overnight until the transparent films peeled off. The luminescence sensing capacity of the final product was evaluated with solutions of different anion types  $(10^{-4} \text{ M})$  in dimethylsulfoxide (DMSO).

Standard procedures were used to calculate means and standard deviations. Image processing was performed with ImageJ ver. 1.44p (NIH, USA).

#### **Results and discussion**

We aimed to synthesize a lanthanide complex-based luminescent sensor for the detection of various anions relevant to biological and environmental processes. The newly synthesized lanthanide complex with electron-donating methoxy groups, Eu-(TTA)<sub>3</sub>-1, is structurally depicted in Fig. 1A. Eu-(TTA)<sub>3</sub>-1 was characterized by NMR and MS and its properties to detect various anions evaluated. The sensor's photophysical properties were determined via UV-vis and fluorescence spectroscopy in DMSO as a solvent. Fig. 1B shows that Eu-(TTA)<sub>3</sub>-1 could be excited by both the 254 and 365 nm excitation wavelengths of a portable ultra-violet light, which resulted in an intense red emission. It further visualizes that responses to various anions and concomitant color changes can easily be detected, even by the human eye. The absolute quantum yield and emission lifetime were determined to be 10% and 1.10 ms for europium ions (Ex = 356 nm) in pure DMSO, respectively.

The luminescent ternary complex Eu-(TTA)<sub>3</sub>-1 was dissolved in DMSO, to a final concentration of  $1 \times 10^{-5}$  M to give a colorless solution with two distinguished UV bands at 283 and 346 nm and a single broad and a series of sharp emission bands (Fig. 2). The peak at 346 nm may be attributed to both the thenoyltrifluoro-acetonate ligands [25] and the phenanthroline ring of ligand **1**.

The absorption at 283 nm is mainly caused by the aromatic moieties or the phenanthroline heterocyclic ring (Fig. 3). Upon titration with 3 equivalents fluoride anions (tetrabutylammonium salt), the two peaks remained relatively stable. However, the aromatic ring of ligand **1** was obviously affected after an eight-fold fluoride addition, as deduced from changes in the spectrum at 283 nm, since this band gradually decreased and concomitantly a new peak at around 294 nm emerged. This indicated that the sensor complex formed hydrogen bonds with fluoride anions at relatively high concentrations. Similar effects were observed during titration of 3–10 equivalents of tetrabutylammonium acetate ([Bu<sub>4</sub>N]<sup>+</sup>AcO<sup>-</sup>) to the sensor complex, indicating interaction with acetate anions and a recognition effect for these (Fig. S1). Further addition, however, caused little change in the absorption curves.



Fig. 2. Absorption and emission spectra of  $1 \times 10^{-5}$  M Eu(TTA)<sub>3</sub>-1 in DMSO. The emission spectrum was recorded by exciting the chromophore at 346 nm.



Fig. 3. UV-vis spectra of  $10^{-5}$  M Eu(TTA)<sub>3</sub>-1 in DMSO in the presence of 0–10 equivalents of fluoride anions.

Analogously, we also measured the binding behavior and affinity of  $HSO_4^-$ ,  $Cl^-$ ,  $Br^-$ ,  $I^-$  and  $H_2PO_4^-$  anions for Eu-(TTA)<sub>3</sub>-**1**. On all occasions the ultra-violet absorption lines remained almost constant at high concentrations, showing that there is insufficient binding to cause changes in the absorption spectrum (Fig. S2).

<sup>1</sup>H-NMR spectroscopy was used to study the anion binding affinity to ligand **1** (Fig. 4). The addition of 5 eq. fluoride anions caused the aromatic protons  $H_d$  of **1** nearest to the imidazole ring (Fig. 1A) to shift to low field (from 7.62 to 7.71 ppm) as a result of the recognition process (Fig. 4). Furthermore, the protons of the phenanthroline ring  $H_a$  and  $H_c$  (Fig. 1A) have enlarged the distances between each other, suggesting that **1** binds fluoride ions via hydrogen interactions. Interestingly, ligand **1** responded not only to fluoride anions, but acetate and  $H_2PO_4^-$  anions could also take part in hydrogen bond formation (Fig. S3).

Previously, we found that an imidazole-ring covalently bound to hydroxyl substituted benzene could recognize fluoride anions stoichiometrically (1:1) [24]. In the current Eu(TTA)<sub>3</sub>-1 complex, the three electron donating methoxy groups (Fig. 1A), which strengthened the electron-rich  $\pi$ -cloud of aromatic ring, directly affect the electron distribution of the adjacent imidazole moiety. As a result, the hydrogen atom of imidazole is much less electron positive and it becomes harder to accept the attack of a lone electron pair from fluoride or other anions. NMR analysis of ligand **1** in combination with HSO<sub>4</sub><sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup> and Cl<sup>-</sup>, but **1** did not give rise to signal changes in each proton (data not shown).

As shown in Figs. 2 and 5, the Eu(III) ternary complex in DMSO solution mainly displays characteristic metal-centered emission. When the emission wavelength was fixed at 615 nm, the excitation spectrum shows a broad band from 250 to 400 nm with two peaks at 275 and 353 nm, which were virtually consistent with their absorption lines (Fig. S4). The shape of the emission spectrum can be interpreted as follows: the excited  ${}^{5}D_{0} \rightarrow {}^{7}F_{J}$  transitions exhibit five main components for J = 0-4, respectively and no splitting of  ${}^{7}F_{J}$  level could be observed. After addition of 3 eq. of fluoride anions, the red emission from europium ions decreased and the blue emission of the ligand changed slightly. As a consequence, we observed a combination of red and blue luminescence resulting in the



Fig. 4. <sup>1</sup>H-NMR spectra measured by titration of a DMSO- $d_6$  solution of pure 1 (1 mM) with 0–5 eq. of [ $Bu_4N$ ]F.



Fig. 5. Emission spectra of 10<sup>-6</sup> M Eu(TTA)<sub>3</sub>-1 in DMSO, excited at 356 nm in the presence of 0–10 eq. of [Bu<sub>4</sub>N]<sup>+</sup>F<sup>-</sup>.

observed purple color shown in Fig. 1B. With increasing addition of fluoride anions, gradual changes in the emission spectrum became apparent culminating in the appearance of a new band centered at 500 nm. Further addition of the same anion beyond 10 eq. did not change the luminescence spectrum significantly.

Similarly, the binding capability of acetate anions was evaluated and upon addition of 3 eq. of acetate anions, the red emission from europium ions almost disappeared and only a broad band from 400 to 550 nm was observed. Interestingly, the blue emission of the ligand (around 450 nm) decreased and a new band around 500 nm increased stepwise (5–10 eq. addition), which again demonstrates that acetate anions were involved in hydrogen bonding (Fig. 6). Accordingly, it is possible to observe green luminescence visually.

Additionally, we investigated the effect of titration of  $Eu(TTA)_3$ -**1** with various concentrations of  $H_2PO_4^-$  on the emission spectrum. In stark contrast to the aforementioned anions, the addition of dihydrogen phosphate to the solution instantaneously quenched the emission of the europium ions (Fig. 7). Concomitantly, the broad band attributed to the phenanthroline ligand dramatically increased in the blue emission region upon addition of  $H_2PO_4^-$  anions. Hence, we could visually observe strong blue luminescence when exciting the solution with UV light (Fig. 1B).

Liu et al. [26] recently reported a calix[4]arene-Ru(II) polypyridine sensor with imidazo[4,5-*f*]-1,10-phenanthroline groups, which displayed bright green emission upon binding of fluoride anions. They argue that deprotonation of the NH group of the imidazole ring causes charge redistributions within the complex and that fluoride anions bind via hydrogen bonds. In our series of experiments, we have observed similar effects and consequently agree with their description of a possible mechanism for the changes in luminescence upon fluoride binding. As for dihydrogen phosphate anion binding, we suggest that the observed luminescence effects are caused by displacement of the phenanthroline ligand by  $H_2PO_4^-$  and as such displays phenanthroline's original blue emission.



Fig. 6. Emission spectra of  $10^{-6}$  M Eu(TTA)<sub>3</sub>-1 in DMSO, excited at 356 nm in the presence of 0–10 eq. of  $[Bu_4N]^+ACO^-$ .



Fig. 7. Emission spectra of  $10^{-6}$  M Eu(TTA)<sub>3</sub>-1 in DMSO, excited at 356 nm in the presence of 0-10 eq. of  $[Bu_4N]^+$  H<sub>2</sub>PO<sub>4</sub><sup>-</sup>.

Analogous experiments were carried out with Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, HSO<sub>4</sub><sup>-</sup> and the emission was monitored as presented in Fig. S5. The previous UV–vis absorption and <sup>1</sup>H-NMR measurements indicated that no hydrogen bonding interactions occurred with these anions, whilst the fluorometry measurements showed that the variation in the europium emission was relatively low in the presence of an excess amount of these anions, suggesting that some quenching of the signal at 615 nm occurred, which was most pronounced for iodide and hydrogen sulfate anions (I<sup>-</sup> > HSO<sub>4</sub><sup>-</sup> > Br<sup>-</sup> ≈ Cl<sup>-</sup>).

To explore the potential of the complexes for electronic, photonic and advanced (bio) imaging applications and to enhance processability and mechanical stability, it is useful to incorporate lanthanide-complex sensors into an inert matrix, such as synthetic polymers. We opted to use poly-methyl methacrylate since this is presently the cheapest and most commonly used support for the development of chemical sensors. Furthermore, PMMA nanoparticles can be synthesized via emulsion polymerization for the delivery of payloads to cells and tissues [27] and, in combination with a luminescent complex, for imaging and sensing purposes. Therefore, we incorporated the europium complex into PMMA via copolymerization from which thick films could be made by casting on a glass support. The resulting composites were all transparent, flexible and robust, and could easily be bent under application of external forces whilst retaining its structural integrity.

We determined that 0.9 mg Eu(TTA)<sub>3</sub>-1/5 ml methyl methacrylate (MMA) doping concentration resulted in optimal emission intensities. Furthermore, both the overall quantum yield (18%) and lifetime of europium (III) ions (1.30 ms) increased in this polymeric matrix compared with the pure complex (Ex = 343 nm). The emission spectra showed significant suppression of the blue emission of the organic ligands, indicating a more efficient energy transfer to the europium complex (Fig. 8). We also studied the initiator concentration dependence of the emission spectra by Eu-complex doping films (Fig. S6). It was observed that the amount of initiator would not induce dramatic luminescence changes when the concentration was less than 0.3%. If it was increased to 0.5%, the emission peak of Eu-complex reduced significantly. It shows that numerous resultant shorter chains (high initiator concentration) may restrict the complexation between Eu(III) ions and the coordination ligands. To test if the films were sensitive to anions and as such detect these, we immersed the films into various DMSO solutions containing a variety of anions  $(10^{-4} \text{ M})$  and determined their luminescence or loss thereof. The red emitting film lost its luminescence only in response to fluoride anions over



Fig. 8. Emission spectra of Eu(TTA)<sub>3</sub>-1 (0.1, 0.5 and 0.9 mg) entrapped in PMMA films ( $\lambda$ ex = 343 nm).



**Fig. 9.** Fluorescence microscopic evaluation of the luminescence of Eu(TTA)<sub>3</sub>-1 (0.9 mg) doped PMMA film. (A) Fluorescence micrograph of the doped film (( $\lambda$ ex = 343 nm) show a homogenous distribution of the complex with some larger clusters. (B) A surface plot of the fluorescence intensities in (A) reveal that in addition to the areas of maximal intensity, significant emission between these exist.

all the others (including acetate and  $H_2PO_4^-$  anion) and turned to an intense purple after a relatively long period of time (10 h). The quenching constant was calculated from the Stern–Volmer equation [28] (Y = 10351X + 1.0281,  $R^2$  = 0.9996, Fig. S7). The limits of

detection (LOD) was measured by LOD = 3SD (standard deviation)/slope of the linear function (LOD here is  $1.45 \times 10^{-5}$  M).

TGA provides a reliable way to measure the thermal stability of europium containing polymers. Polymer films are subject to temperatures less than 180 °C in daily practical use. The europium complex doped PMMA films showed a significantly higher thermal stability compared with the pure complex (Fig. S8). According to Wang et al. [21], the coordination number of europium ions was unsaturated and further complexation between oxygen atoms of the methacrylate moiety and europium ions will occur. This cross-linking effect reduces the flexibility of the polymer chains and concomitantly the decomposition temperature will increase.

Fluorescence microscopic evaluation of the film revealed an overall homogenous bright red luminescent signal (Fig. 9A), which clearly confirms the presence of the europium complex in the PMMA matrix. The lanthanide complex was homogeneously dispersed within the polymer matrix (Fig. 9A and B) and assembled into large aggregates with average diameters from 30–50  $\mu$ m and seldom large than 100  $\mu$ m, which nonetheless led to a homogenous signal (Fig. 9B). Overall, approximately 70% of surface area, as calculated from Fig. 9B, showed emission intensities above 0.4 normalized emission, of which 28% exhibited the maximum intensity emission.

### Conclusions

With the intention of exploiting the unique properties of lanthanide luminescence and based thereon to synthesize a sensor sensitive to different types of relevant anions, we prepared a red luminescent ternary europium-chromophore-sensing ligand complex (ternary europium (III) tris(2-thenoyltrifluoroacetonate) with 2-(3,4,5-trimethoxyphenyl)imidazo[4,5-f]-1,10-phenanthroline ligands). The sensor itself exhibited a bright red luminescence with an absolute quantum yield of 10% and a lifetime of 1.10 ms. In response to fluoride anions this color changed to an intense purple color and upon acetate titration gave rise to light green emission. Additionally, for the first time, we developed a sensor of this type capable of recognizing  $H_2PO_4^-$  via a sharp change to blue luminescence. The addition of excess amounts of Br<sup>-</sup>, I<sup>-</sup> and Cl<sup>-</sup> showed no shift in the emission maxima with only minor quenching of the major emission bands. Europium complex doped polymeric PMMA films not only guaranteed mechanical robustness, but showed a strong red luminescent signal that responded to fluoride anions and as such could be used as fluoride sensor. Further validation studies, including the application of the sensor to real-time monitoring, establishing the *in situ* detection limit, and development of various applications of the probe are currently underway.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2012.05.064.

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