

FULL PAPER

Red Light Emission of POSS Triol Chelated with Europium

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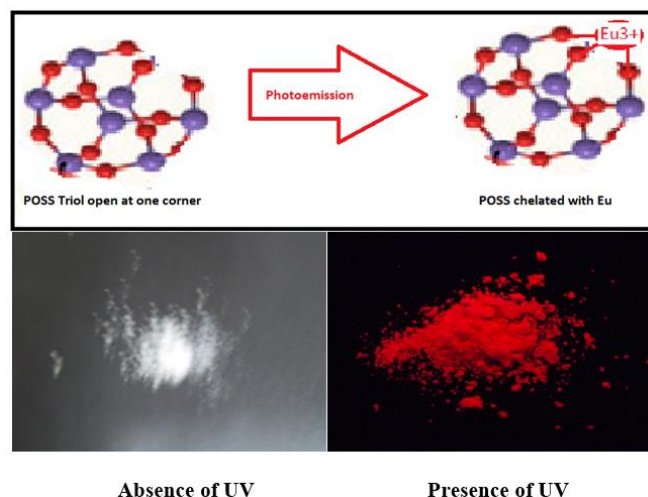
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ABSTRACT: The europium silsesquioxane complexes are synthesized with $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ to corner cap with incomplete condensation of hepta(3,3,3-trifluoropropyl)-tricycloheptasiloxane trisodium silanolate (7F-T7-(ONa)₃) along with the 1,3,5,7,9,11,14-hepta isobutyltricyclo [7,3,3,15,14] heptasiloxane-3,7,11-trisilanol (trisilanolisobutyl-POSS). These europium silsesquioxane complexes are highly soluble in organic solvents and show a red emission. Photoluminescence of Eu^{3+} -CF-POSS is higher compared with Eu^{3+} -CH-POSS. This fluorescence enhancement is due to the significant effect of the large POSS units. The europium silsesquioxane complexes were characterized by Fourier transform infrared spectrophotometer (FT-IR), field emission scanning electron microscopy (FE-SEM), energy dispersive X-ray analysis (EDX) and thermogravimetric analysis (TGA). The excitation and emission pattern of polyhedral europium silsesquioxanes was studied using photoluminescence spectrophotometer. The results show an excellent emission property at the wavelength between 612 and 620 nm which correspond to the $^5\text{D}_0$ - $^7\text{F}_2$ transition of europium in polyhedral silsesquioxanes.

KEYWORDS: Hepta(3,3,3-trifluoropropyl)-tricycloheptasiloxane trisodium silanolate (7F-T7-(ONa)₃); trisilanolisobutyl-POSS; Photoluminescence; Eu^{3+} .

GRAPHICAL ABSTRACT:



1. Introduction

In recent years, organic-inorganic hybrid materials paid a growing interest in the development of novel light-emitting

materials for their challenging mechanical, thermal, and chemical stability [1-4]. It is difficult to generate luminescence by direct excitation of the lanthanide ion because the absorption bands are weak and narrow [5]. In general, lanthanide ions are chelated with

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organic ligands to enhance absorption by forming broad and intense absorption bands [6]. Hence the metal-centered luminescence is originated from the intramolecular energy transfer through the excited state of the ligand to the emitting level of the lanthanide (antenna effect) [7].

Polyhedral oligosilsesquioxanes of the general formula $(\text{RSiO}_{1.5})_n$ form an unusual and concerning class of organosilicon compounds, which currently have a strong impact on both catalysis research [8,9] and materials science [10]. Besides catalysis research the chemistry of metallasilsesquioxanes also receives considerable current interest [11].

The concept of studying polyhedral metallasilsesquioxanes to mimic surface sites in heterogeneous silica-supported transition metal catalysts was first proposed by Feher [12]. In materials science, certain metallasiloxanes are of interest as molecular precursors for metal-containing inorganic polymers [13] and other new materials [14–15]. There are many examples of the well-characterized silsesquioxane derivatives of rare-earth metals [16–18], a tetrameric neodymium silsesquioxane complex was prepared [19].

Silsesquioxane complexes of M^{3+} ions show varied coordination chemistry due to the facially capping geometry imposed by the silsesquioxane ligand a monomeric complex in the absence of other donors would result in a “bare” metal ion. The highly electrophilic nature of such a complex may results in formation of variety structures and the exact structure of this complexes was not determined.

Based on our continues work on POSS-based luminescent hybrid material for enhanced photo-emitting properties [20], here we are reporting the synthesis of europium silsesquioxane with trisodium fluorinated silsesquioxane **1** (Eu^{+3} -CF-POSS) and (Eu^{3+} -CH-POSS) triol of isobutyl silsesquioxane **2** (Figure 1). In these complexes, europium exist as Eu^{3+} which shows effective photoluminescence property with an emission of red color and so, these are homogeneous metal containing silsesquioxanes [9]. The existence of Eu^{3+} was confirmed by excitation spectrum with 395, 466 & 533 nm due to the transitions of ${}^7\text{F}_0$ – ${}^5\text{D}_4$, ${}^5\text{G}_2$, ${}^5\text{L}_6$, ${}^5\text{D}_3$ of Eu^{3+} .

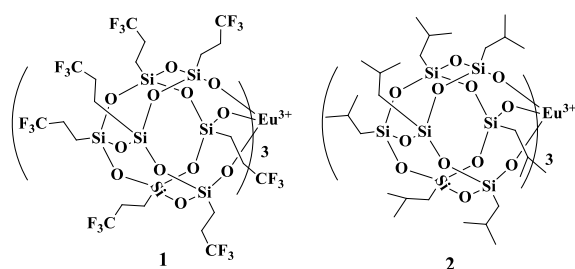


Fig. 1. Eu^{3+} -CF-POSS (1) and Eu^{3+} -CH-POSS (2)

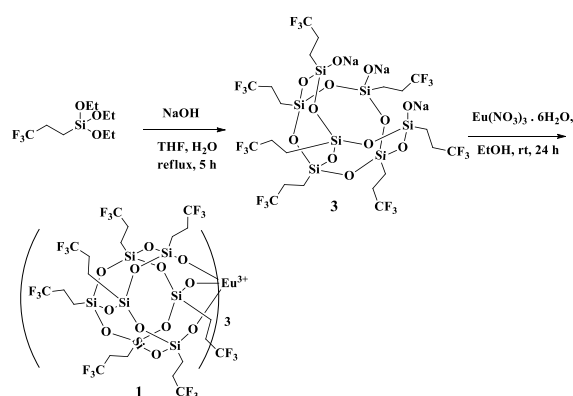
2. Materials and methods

Triethoxy(3,3,3-trifluoropropyl)silane, isobutyltrimethoxysilane, and $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were purchased from Aldrich (USA) and used without further purification. All other reagents and solvents were purchased from TCI Chem. Ltd. (Japan).

Isobutyltrimethoxysilane (23.325 g, 130.8 mmol), acetone (100 mL), distilled water (2 g, 111 mmol), and $\text{LiOH} \cdot \text{H}_2\text{O}$ (2.5 g, 59.55 mmol) were charged in a three-necked flask equipped with a reflux condenser and a magnetic stirrer. The mixture was refluxed in an oil bath for 20 h with vigorous stirring and was acidified by quenching it into 1 mol L^{-1} HCl (aq) (100 mL) and stirring for 2 h. The resulting solid was filtered and washed two times with CH_3CN (2 x 80 mL) and air dried. 16.18 g of the product was isolated in 73.8% yield (Scheme 1).

^1H NMR (CDCl_3 , 400 MHz) of **4**: δ (ppm) 6.66 (bs, 3H, OH), 1.91-1.78 (m, 7H, -CH-),

0.98-0.92 (m, 42H, $(\text{CH}_3)_2$) and 0.64-0.54 (m, 14H, $-\text{CH}_2-$).

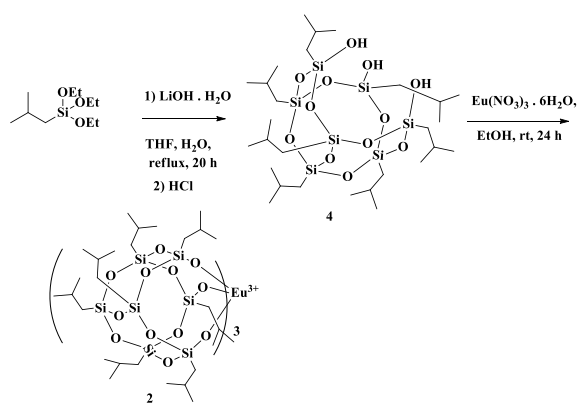


Scheme 1. Synthesis of Eu^{3+} -CF-POSS

A two-necked flask equipped with a reflux condenser and a thermometer was charged with (3,3,3-trifluoropropyl) trimethoxysilane (5 g, 22.93 mmol), THF (20 mL), distilled water (619 mg, 34.4 mmol), and sodium hydroxide (450 mg, 11.46 mmol). The mixture was refluxed in an oil bath thermostatic at 70 °C for 5 h with magnetically stirring. The system could get cool to room temperature and left for 15 h. The volatile components were removed by heating at 95 °C under atmospheric pressure to obtain a white precipitate, which was collected by a membrane filter having a pore diameter of 0.5 μm , washed with THF, and dried at 80 °C for 3 h in a vacuum oven to yield hepta(3,3,3-trifluoropropyl)-tricycloheptasiloxane trisodium silanolate (7F-T7-(ONa)₃), as a white powder in a quantitative yield. ^1H NMR (CD_3OD , 400

MHz) of **3**: δ (ppm) 2.39-2.1 (m, 14H, -CH₂-) and 0.98-0.60 (m, 14H, -CH₂)

Trisodium silanolate POSS or trisilanol isobutyl-POSS (0.069 mmol) was dissolved in 2 mL absolute ethanol while stirring, and Eu(NO₃)₃·6H₂O (0.023 mmol) was added to the solution. After 16 h solvent was removed by vacuum rotary evaporator to obtain a white solid (Scheme 1 & 2). The white solid was washed with water (2 mL) and then dried. The complex formation was further monitored by exposing the obtained white solid under UV light to observe red emission.



Scheme 2. Synthesis of Eu³⁺-CH-POSS.

The FT-IR (FT-IR-6300 Spectrometer, JASCO, Japan) of all the samples were performed between 400 and 4000 cm⁻¹ with the resolution of 0.07 cm⁻¹. Initially, the samples were finely grounded with KBr and made as a pellet by applying pressure on it. The pellets were kept in the instrument and recorded the spectrum with the average scans of 10. The ¹H NMR (Avance 400,

Bruker, Germany) of all synthesized samples were achieved to elucidate the structure by using CDCl₃ as solvent. The surface morphology was studied using a field-emission scanning electron microscope (FE-SEM, MIRA II, TESCON, Czech), and was performed by placing the sample on carbon tape which had been further coated with platinum. The applied voltage was kept at 20 kV for all the analysis. The elemental distribution (Oxford, USA) was performed using energy dispersive X-ray analysis to confirm the presence of europium in the sample. The excitation and emission properties of the europium conjugated samples were performed using photoluminescence spectrophotometer (RF-5301, Shimadzu, Japan).

3. Results and Discussion

The Eu³⁺-CF-POSS and Eu³⁺-CH-POSS complexes were synthesized by the above experimental procedures. Complexes were characterized by FT-IR, thermogravimetric analysis (TGA), FE-SEM, energy dispersive X-ray analysis (EDX), and photoluminescence spectrophotometer.

In the FT-IR spectrum of Eu-CF-POSS (Figure 2a and Figure 2b) a very strong band at 1129 cm⁻¹ is attributable to the ν

(Si–O–Si) vibrations, whereas a peak at 1253 cm^{-1} provided some indication for the presence of an –Si–C functionality, The characteristic bands between 2873 and 2956 cm^{-1} are due to the vibration frequency of the C–H bond. In the IR spectrum of (7F-T₇-(ONa)₃) the characteristic absorption peaks of Si–O–Si (1116 cm^{-1}) and Si–C

(1229 cm^{-1}) are much strong than hydrocarbon and some peaks of C–C (1333 cm^{-1}) are covered. The peak (2954 cm^{-1}) indicates the C–H structure of methyl. The absorption peak at 1445 cm^{-1} could be assigned to Eu³⁺-CF-POSS by Si–O–Eu ν (1455 cm^{-1}) [21].

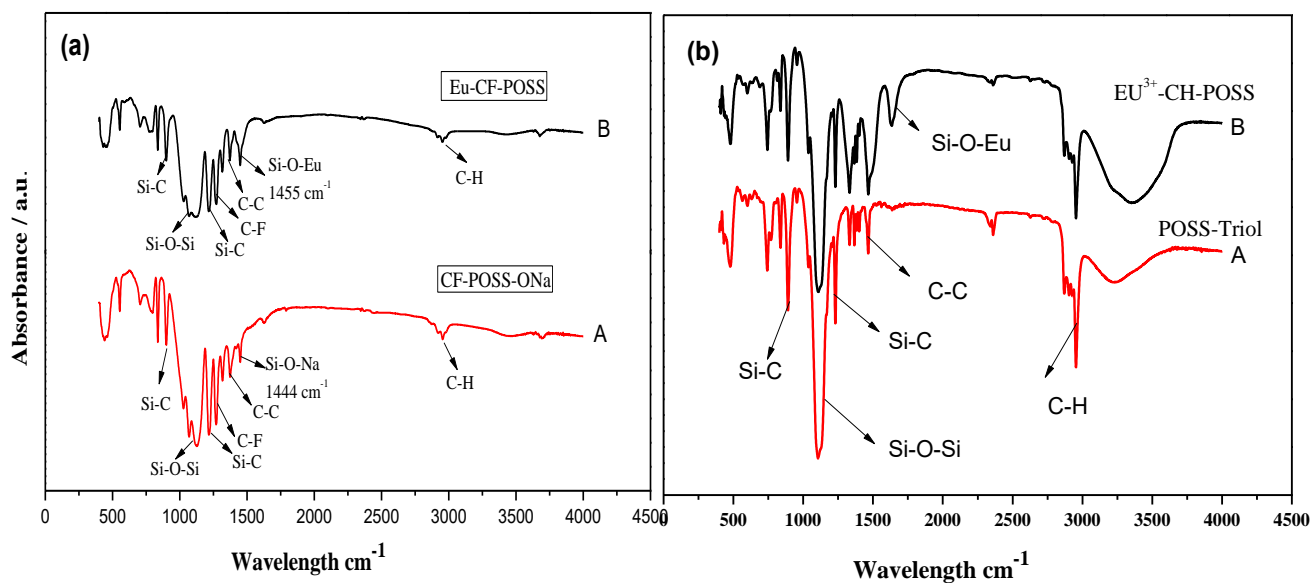


Fig. 2. FT-IR spectra of (a) europium free (7F-T₇-(ONa)₃) (A) and Eu³⁺-CH-POSS (B); (b) POSS triol (A) and Eu³⁺-CH-POSS (B).

The thermal stability of the hybrid Eu³⁺ silsesquioxane complexes was investigated by TGA measurement. Thermogravimetric profiles of Eu³⁺-CF-POSS and Eu³⁺-CH-POSS hybrid materials are shown in Figure 3a and 3b, respectively. From TGA curves, weight loss of Eu³⁺-silsesquioxane complexes starts around 57 to 150 °C and is

might be attributed to desorption of physically adsorbed water and the residual solvent. The Eu³⁺-CF-POSS hybrid material shows a major weight loss of 80% between 250 and 390 °C. This is attributed to the thermal degradation of organ silicate framework, involving C–F and C–C bond cleavage. The minor weight loss at 635 °C

(Figure 3a) is due to thermal degradation of Si–C bond cleavage. The weight loss occurred in hybrid material at 670 °C (Figure 3b) might be due to the loss of the SiO₂ residuals. There is no significant further weight loss in hybrid material when the temperature was above 670 °C. Hence, from the TGA analysis, the hybrid Eu-CF-POSS was found to be thermally stable up to 250 °C.

The FE-SEM images of Eu³⁺-CF-POSS and Eu³⁺-CH-POSS complexes are shown in Figure 4. From the SEM image of Eu³⁺-CF-POSS (Figure 4a) many particles observed in hard surface are resulted in chelation of europium in fluorinated POSS trisodium. The SEM image of Eu³⁺-CH-POSS (Figure 4b) shows the formation of bunches has been clearly observed. These bunches contain smaller microstructure.

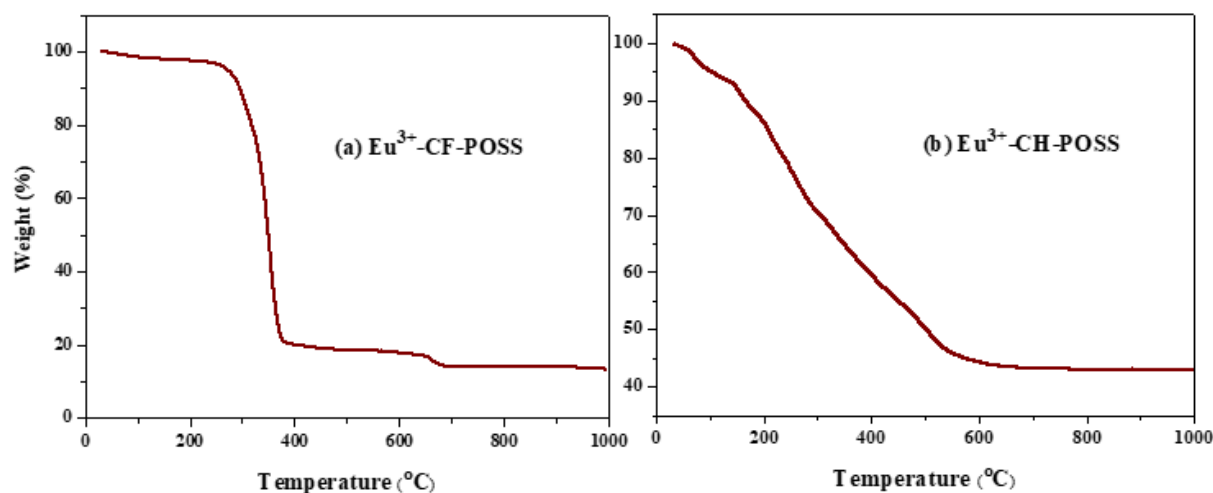


Fig. 3. TGA curve of (a) Eu³⁺-CF-POSS; (b) Eu³⁺-CH-POSS.

In addition to this, the homogeneous morphology on the surface of the hybrid powders can be clearly observed. This might be attributed to the chemical bonding of each component and molecular level hybridization of the organic and inorganic species. The SEM image of Eu³⁺-CH-POSS hybrid materials demonstrates that europium complexes were chelated with isobutyl POSS triol uniformly due to covalent bonds bridged between different

phases and they were composed quite uniformly so two phases can exhibit their distinct properties together.

The EDX analysis of both Figure 4a and 4b clearly implies presence of Eu, N, Si and O elements over the entire region of the surface. The clusters containing 'Eu' play major role in the photoluminescence emission.

The europium doped silsesquioxanes shows a strong red photoluminescence upon radiation with ultraviolet light. The excitation and emission spectra of Eu^{3+} -CF-POSS and Eu^{3+} -CH-POSS materials recorded using a fluorescence spectrophotometer. Initially, the excitation spectra of Eu^{3+} -CF-POSS and Eu^{3+} -CH-POSS were recorded at 617 nm and 618 nm (Figure 5). Broad bands centered at about 250 and 343 for Eu^{3+} -CF-POSS (Figure 5a), and 360 nm for Eu^{3+} -CH-POSS (Figure 5b) were observed and these broad bands may

arise from the charge transfer transition between POSS moiety and Eu^{3+} [20]. Some sharp peaks originating from f-f transitions of Eu^{3+} can also be observed in the longer wavelength region at 395, 466 & 533 nm due to the transitions of ${}^7\text{F}_0$ - ${}^5\text{D}_4$, ${}^5\text{G}_2$, ${}^5\text{L}_6$, ${}^5\text{D}_3$ of Eu^{3+} . The excitation energy at 395 and 466 nm was used to excite the electrons from valence band to conduction band for both Eu^{3+} -CF-POSS and Eu^{3+} -CH-POSS complexes. Upon excitation at 343, 395 and 466 nm, the characteristic transition lines from the excited ${}^5\text{D}_0$ level of Eu^{3+} detected

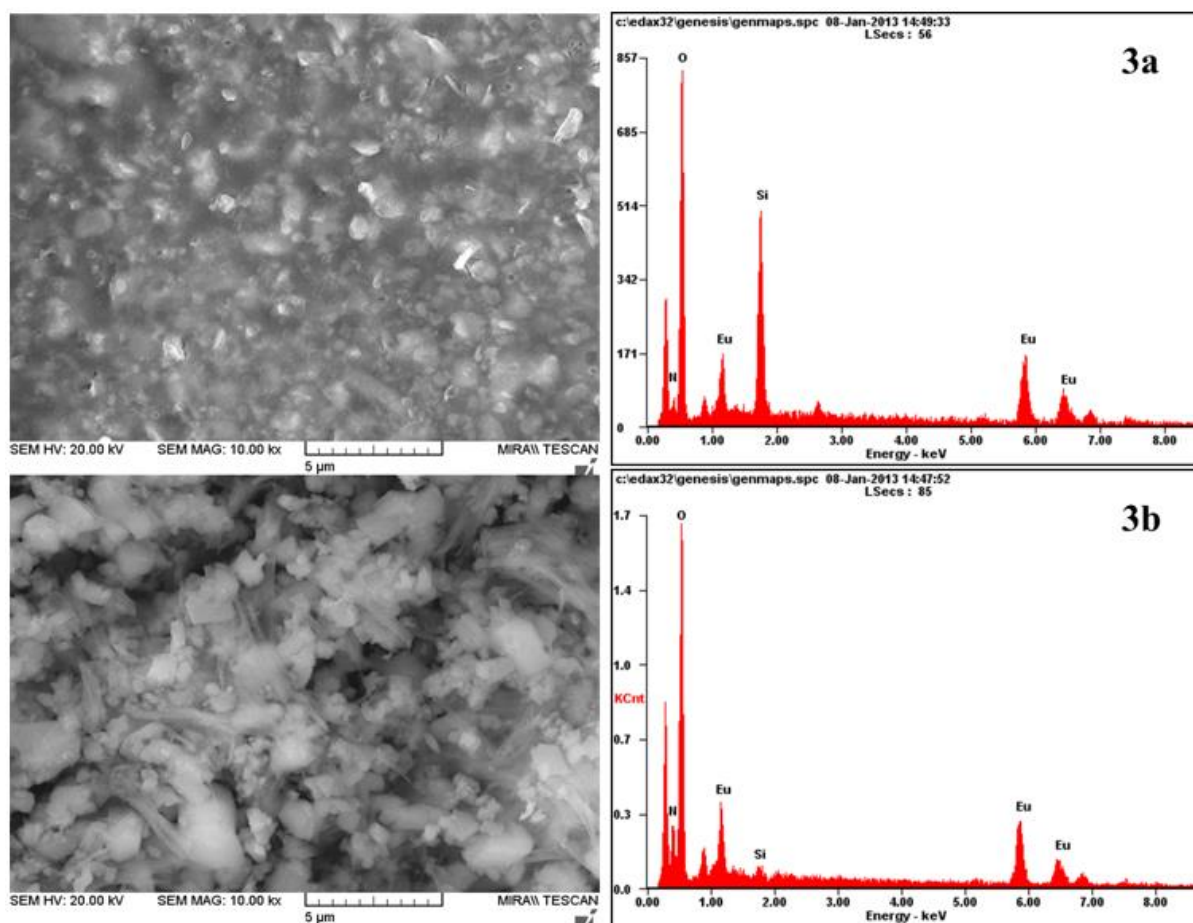


Fig. 4. Scanning electron micrographs of (a) Eu^{3+} -CF-POSS and its EDXA; (b) Eu^{3+} -CH-POSS and its EDXA.

The europium doped silsesquioxanes shows a strong red photoluminescence upon radiation with ultraviolet light. The excitation and emission spectra of Eu^{3+} -CF-POSS and Eu^{3+} -CH-POSS materials

recorded using a fluorescence spectrophotometer. Initially, the excitation spectra of Eu^{3+} -CF-POSS and Eu^{3+} -CH-POSS were recorded at 617 nm and 618 nm (Figure 5).

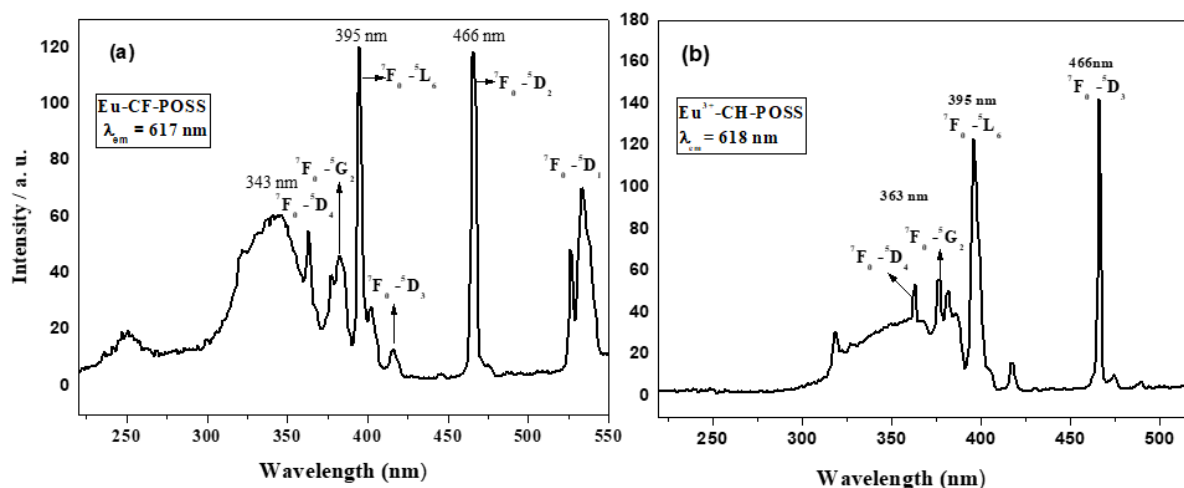


Fig. 5. Excitation spectra of (a) Eu^{3+} -CF-POSS; (b) Eu^{3+} -CH-POSS.

Broad bands centered at about 250 and 343 for Eu^{3+} -CF-POSS (Figure 5a), and 360 nm for Eu^{3+} -CH-POSS (Figure 5b) were observed and these broad bands may arise from the charge transfer transition between POSS moiety and Eu^{3+} [20]. Some sharp peaks originating from f-f transitions of Eu^{3+} can also be observed in the longer wavelength region at 395, 466 & 533 nm

due to the transitions of ${}^7\text{F}_0\text{--}{}^5\text{D}_4$, ${}^5\text{G}_2$, ${}^5\text{L}_6$, ${}^5\text{D}_3$ of Eu^{3+} . The excitation energy at 395 and 466 nm was used to excite the electrons from valence band to conduction band for both Eu^{3+} -CF-POSS and Eu^{3+} -CH-POSS complexes. Upon excitation at 343, 395 and 466 nm, the characteristic transition lines from the excited ${}^5\text{D}_0$ level of Eu^{3+} detected in the emission spectra (Figure 6).

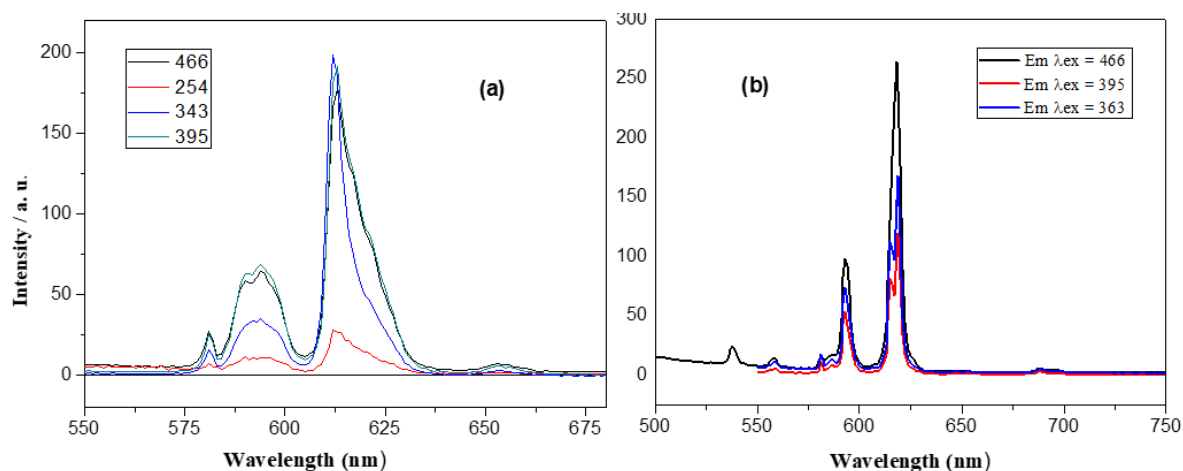


Fig. 6. Emission spectra of (a) Eu^{3+} -CF-POSS; (b) Eu^{3+} -CH-POSS.

It is well known that the emission spectrum of Eu^{3+} ion consists of lines in the red spectral region [22]. These lines have found an important application in lighting and display devices and they correspond to transition from excited $^5\text{D}_0$ level to the $^7\text{F}_J$ ($J=1-4$) levels of the $4f^6$ configuration [23]. The splitting of the emission transitions yields the crystal field splitting of the $^7\text{F}_J$ levels, while the $^5\text{D}_0$ level is not splitted by the crystal field (because $J=0$). If the location of Eu^{3+} shows absence of inversion symmetry, the electric-dipole transitions are no longer strictly forbidden and appear as lines in the spectra. Thus, some transitions, with $\Delta J=0, \pm 2$, are hypersensitive $^5\text{D}_0-^7\text{F}_2$ emission transition is most dominative compared to the other transitions [24].

As shown in the photoluminescence spectrum, of Eu^{3+} -CF-POSS (Figure 6a) all the emission lines observed at 581, 595,

618, 649 and 700 nm. For Eu^{3+} -CH-POSS (Figure 6b) all the emission lines observed at 558, 581, 592, 619 and 690 nm are well correlated to the characteristic emission of the rare earth Eu^{3+} ion which corresponds to the relaxation of the excited state $^5\text{D}_0$ to the different levels of the ground states ($^7\text{F}_J$). From the photoluminescence spectrum, among all transitions, the hypersensitive transition corresponding to $^5\text{D}_0-^7\text{F}_2$ transition gives strongest emission. This indicates that Eu^{3+} occupies a site with low symmetry.

There are no emission corresponding to the organic ligands (no band observed in blue or green spectral regions), which confirms that the surrounding organic ligands absorb and transfer energy efficiently to the central Eu^{3+} ions. Among the five transitions, the $^5\text{D}_0-^7\text{F}_0$ transition ($0-0$ transition) is a forbidden transition and

the ${}^5D_0-{}^7F_1$ transition belongs to magnetic dipole transition, whereas all other transitions belong to electric dipole transitions. The presence of single peak of ${}^5D_0-{}^7F_0$ transition reinforces that all Eu^{3+} experiences single local environment in both the hybrid materials. The intensities of magnetic dipole are independent of the chemical surroundings of Eu^{3+} ion. Luminescence properties of the Eu^{3+} -CF-POSS and Eu^{3+} -CH-POSS compound containing POSS moiety showed intense luminescence with high color purity in turn Eu^{3+} -CF-POSS complex exhibited more intense luminescence. The reason for high intensity may be due to the high packing density of phosphor in POSS. All these results confirm the crucial role of POSS in the improvement of functional properties. The intense luminescence and high thermal

stability suggests that Eu^{3+} -CF-POSS and Eu^{3+} -CH-POSS is suitable candidate for the luminescence applications. This means that the emitted light has a pure red color.

4. Conclusions

In summary, this work reports photoluminescence of europium silsesquioxanes complexes (Eu^{3+} -CF-POSS & Eu^{3+} -CH-POSS) prepared from 7F-T7-(ONa)₃ and trisilanolisobutyl-POSS and complexed with rare earth metal europium. Here we are reporting photoluminescence property with lanthanide metal (europium) with an effective red color emission. Due to the presence of fluorine in the POSS moiety the photoluminescence of Eu^{3+} -CF-POSS is higher than Eu^{3+} -CH-POSS shown in Figure 7.

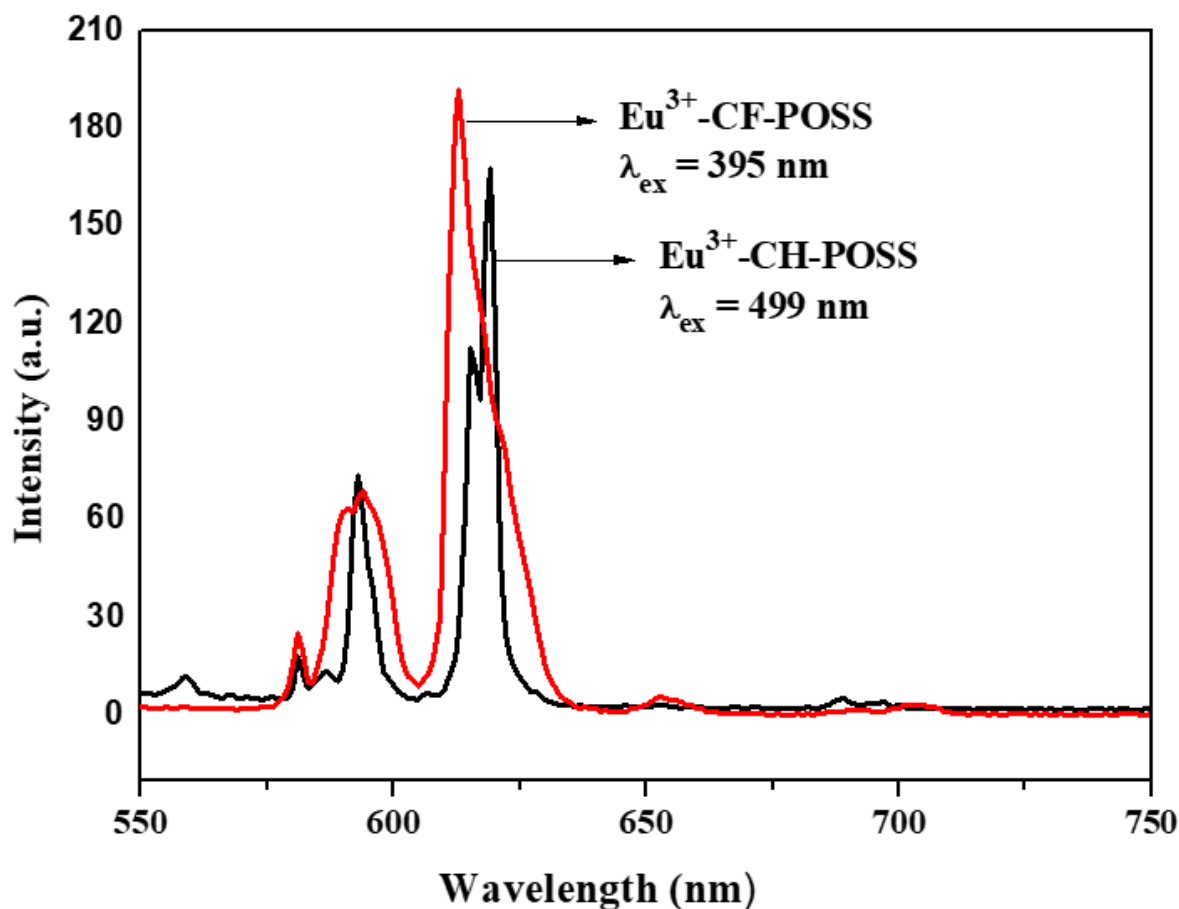


Fig. 7. Emission spectra of the hybrid Eu^{3+} -CF-POSS and Eu^{3+} -CH-POSS.

These complexes are homogeneous in organic solvents such as ethanol, CH_3CN , DMF, etc in electro-optic material applications. Incorporation of POSS moieties not only effectively improves the solubility of the europium silsesquioxanes complexes, but also prevents the fluorescence quenching effect caused by intermolecular aggregation. Crystal formation was not clear. Structural elucidation was not done only we give predicted structure of europium silsesquioxanes complexes. In europium

silsesquioxanes complexes the existence of Eu^{3+} was confirmed by excitation spectrum in which all the emission lines observed at 558, 581, 592, 619 and 690 nm are well correlated to the characteristic emission of the rare earth Eu^{3+} ion.

Acknowledgments

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References

- [1] Friend RH, Gymer RW, Holmes AB, Burroughes JH, Marks RN, Taliani C, Bradley DDC, Santos DAD, Bre JL, ogdlund ML, Salaneck WR (1999) *Nature* 397:121-128.
- [2] Cao Y, Parker ID, Yu G, Zhang C, Heeger AJ (1998) *Nature* 397:414-417.
- [3] Hide F, Diaz-Garcia MA, Schwartz BJ, Anderson MR, Pei Q, Heeger AJ (1996) *Science* 273:1833-1836.
- [4] Lis S, Elbanowski M, Makowska B, Hnatejko Z (2002) *J. Photochem. Photobiol. A* 150:233-247; deSa GF, Malta OL, deMelloDonega C, Simas AM, Longo RL, Santa-Cruz PA, DaSilva Jr EF (2000) *Coord. Chem. Rev.* 196:165-195.
- [5] Green WH, Le KP, Grey J, Tiffani AT, Sailor MJ (1997) *Science* 276:1826-1828.
- [6] Robert CL, Lidia MV, Margie CB, Sean Y (2006) *Cytometry Part A* 69A:767-778.
- [7] Alpha B, Ballardini R, Vincenzo B (1990) *Photochem. Photobiol.* 52:409-416.
- [8] Hanssen RWJM, van Santen RA, Abbenhuis HCL (2004) *Eur. J. Inorg. Chem.* 4:675-683; Lorenz V, Edelmann FT (2004) *Z. Anorg. Allg. Chem.* 630:1147-1157.
- [9] Abbenhuis HCL (2000) *Chem. Eur. J.* 6:25-32.
- [10] Harrison PG (1997) *J. Organomet. Chem.* 542:141-183.
- [11] Volker L, Steffen B, Frank TE (2008) *Z. Anorg. Allg. Chem.* 634:2819-2824.
- [12] Feher F (1986) *J. Am. Chem. Soc.* 108:3850-3852; Volker L, Axel F, Stephan G, John WG, Frank TE (2000) *Coord. Chem. Rev.* 206-207:321-368.
- [13] Borisov SN, Voronkov MG, Lukevits EY (1970) *Organosilicon Heteropolymers and Hetero Compounds*, Plenum, New York; Saam JC in: Zeigler JM, Fearon FWG (Eds.) (1990) *Silicon Based Polymer Science, Advances in Chemistry* 224, American Chemical Society, Washington.
- [14] Sigel GA, Bartlett RA, Decker D, Olmstead MM, Power PP (1987) *Inorg. Chem.* 26: 1773-1780.
- [15] Hrcir DC, Skiles GD (1988) *J. Mater. Res.* 3:410-412.
- [16] Murugavel R, Voigt A, Walawalkar MG, Roesky HW (1996) *Chem. Rev.* 96:2205-2236.

- [17] Herrmann WA, Anwander R, Dufaud V, Scherer W (1994) *Angew. Chem., Int. Ed.* 33: 1285-1286.
- [18] Gun'ko YK, Reilly R, Edelman FT, Schmidt HG (2001) *Angew. Chem., Int. Ed.*, 40: 1279-1281; Stefano M, Fabio C, Enrico B (2014) *New J. Chem.* 38:2480-2485.
- [19] Wu G, Chen Y, Xu DJ, Liu JC, Sun W, Shen Z (2009) *J. Organomet. Chem.* 694:157-160.
- [20] Prem Kumar B, Vijay Kumar BVD, Raghavan CM, Harshavardhan SJ, Yi SS, Gandhi S, Jian zhuang J, Kiwan J, Shin DS (2013) *J Mater Sci* 48:7533-7539.
- [21] Neli M, Makoto T, Kohtaro O (2007) *Organometallics* 26:1402-1410.
- [22] Kłonkowski AM, Szałkowska I, Lis S, Hnatejko Z (2008) *Opt. Mater* 30:1225-1232.
- [23] Blasse G, Grabmaier BC, *Luminescent Materials*, Springer-Verlag, Berlin, 1994, 41 p.
- [24] Nazarov MV, Jeon DY, Kang JH, Popovici EJ, Muresan LE, Zamoryanskaya MV, Tsukerblat BS (2004) *Sol. Stat. Commun.* 131:307-311.

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