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Luminescent liquid

The First Europium(III) β-Diketonate Complex Functionalized Polyhedral Oligomeric Silsesquioxane

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Abstract: The first europium(III) β-diketonate complex functionalized polyhedral oligomeric silsesquioxane (POSS) has been obtained by immobilization of such a complex at a silicon vertex of the POSS cage through the complexation of Eu^{3+} ions with thenoyltrifluoroacetone-functionalized POSS. The new molecular hybrid material is liquid at room temperature, and shows bright-red emission when irradiated with UV light due to energy transfer from the thenoyltrifluoroacetone ligand to the coordinated Eu^{3+} ions. Thermal analysis has revealed a significant improvement in the thermal stability of the material compared with tris(2-thenoyltrifluoroacetonate)europium(III) dihydrate, $[Eu(TTA)_3]\cdot 2H_2O$. In the context of recent advances in printable electronic technology, this novel luminescent organic liquid with the characteristic emission of Eu^{3+} may potentially be useful in the development of next-generation organic devices such as flexible displays.

1. Introduction

Polyhedral oligomeric silsesquioxane (POSS) has been the subject of intensive study due to its well-defined rigid inorganic silica-like core and easily modifiable organic pendant groups. It gives rise to a family of hybrid molecules with an inorganic core made up of silicon and oxygen (Si_8O_{12}) and eight variable organic side groups appended at each silicon vertex of the cage. The overall structures are of size 1–3 nm.[1–6] These POSS derivatives can be tailored for various applications, such as coatings,[7] nanocomposites,[8–11] catalysis,[12–14] porous materials,[15–17] drug delivery,[18,19] and self-assembled structures,[20–23] through appropriate functionalization of the core structure. Recent studies have demonstrated the importance of POSS derivatives in novel applications in photonics and electroluminescent (EL) devices.[24–29] Improved thermal stability, brightness, and external quantum efficiency can be obtained for EL devices when semiconducting polymers are covalently linked to POSS moieties. The solubility, luminescence efficiency, and color purity of conjugated polymers are also significantly improved. The use of dye-functionalized POSS in highly efficient and photostable photonic systems has also been reported.[30–34] These new optical hybrid molecular materials overcome some of the most important limitations intrinsic to sol–gel hybrid composites, while maintaining the combined physical, chemical, and mechanical advantages of organic–inorganic systems.[30]

Lanthanide(III) β-diketonate complexes are interesting luminescent materials for applications in molecular devices.[35–40] Processable lanthanide-based luminescent materials can be realized by incorporating lanthanide complexes into different types of host matrices, such as zeolites,[41–43] inorganic–organic hybrid materials,[35,36,39,44–46] liquid crystals,[47,48] ionic liquids,[49–52] ionogels,[53–59] and polymers.[60–62] However, there have not been any reports on the luminescence of lanthanide complexes in POSS derivatives. Herein, we report a novel kind of luminescent organic–inorganic hybrid liquid material, which was prepared by grafting a europium(III) β-diketonate complex at a corner vertex of the POSS molecule. This was achieved by complexation of Eu^{3+} ions with a thenoyltrifluoroacetone-functionalized POSS, which was in turn synthesized by a corner-capping reaction of a commercially available trisilanol compound (T-heptasiloxane-triol) with a silylated thenoyltrifluoroacetone (Si-TTA), as shown in Scheme 1. To the best of our knowledge, this is the first report of the covalent grafting of a europium(III) β-diketonate complex at a corner vertex of molecular organic–inorganic POSS. It is noteworthy that the obtained europium(III) complex functionalized POSS is a viscous liquid at room temperature. As is well known, room temperature luminescent liquids have been regarded as a new generation of organic soft materials due to their obvious advantages, such as high stability, versatile optical properties, solvent-free fluid behavior, and suitability as host materials for dye molecules.[63] The availability of these novel organic liquids, coupled with recent advances in printable electronic technology, suggests great potential for the development of next-generation organic devices such as flexible displays.[64] Moreover, a room temperature ionic liquid consisting of an octacarboxyl POSS

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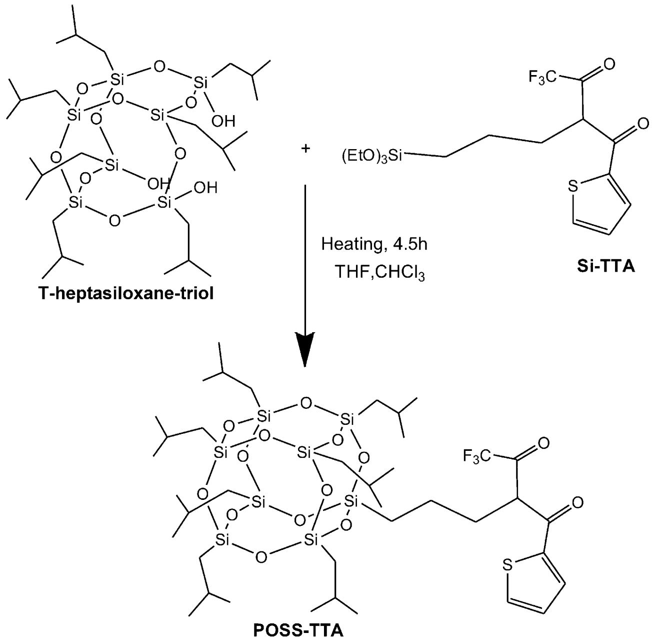


Scheme 1. Synthesis of the thenoyltrifluoroacetone-functionalized POSS, POSS-TTA.

anion and an imidazolium cation has recently been reported.[65]

2. Experimental Section

Materials

2-Thenoyltrifluoroacetone (99%, Aldrich), 3-chloropropyltriethoxysilane (97%, Aldrich), and tricyclo[7.3.3.15,11]heptasiloxane-3,7,14-triol-1,3,5,7,9,11,14-heptakis(2-methylpropyl) (T-heptasiloxane-triol, Aldrich) were used as received. Eu_2O_3 was purchased from Shanghai Yuelong. Europium chloride hexahydrate ($EuCl_3{\cdot}6H_2O$) was obtained by dissolving Eu_2O_3 in hydrochloric acid (37%), removing the excess acid by dilution with water, and concentrating to dryness; this process was repeated several times. The triethoxysilylated molecule (Si-TTA) was synthesized and characterized according to the reported method.[66]

Synthesis of POSS-TTA: In a typical synthesis, a solution of Si-TTA (229.0 mg) in THF (1 mL) was added to a solution of T-heptasiloxane-triol (402.5 mg) in $CHCl_3$ (30 mL). The mixture was heated at 60 °C for 4.5 h under the protection of an inert gas atmosphere. After concentration and washing with methanol, a colorless viscous liquid was obtained. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 5.911$ (t, 1H), 5.380 (t, 1H), 3.119 (s, 2H), 3.002 (d, 1H), 1.798 (m, 9H), 1.310 (m, 2H), 0.905 (d, 42H), 0.538 ppm (d, 16H); elemental analysis calcd (%) for $C_{39}H_{74}F_3O_{14}SSi_8$ (1080.66): C 43.34, H 6.89, S 2.96; found: C 42.72, H 7.02, S 2.90.

Synthesis of the molecular organic–inorganic hybrid material $(POSS\text{-}TTA)_3Eu$: A solution of POSS-TTA (0.153 mmol) in $CHCl_3$ (5.0 mL) was added to a solution of $EuCl_3{\cdot}6H_2O$ (0.051 mmol) in EtOH (5.0 mL). The reaction mixture was heated at 70 °C under stirring overnight. The solvents were then evaporated, leaving a viscous liquid. The liquid product was dried under vacuum at 60 °C overnight. $(POSS\text{-}TTA)_3Eu$ was thereby obtained as viscous liquid. Yield: 80%. Elemental analysis calcd (%) for $EuC_{117}H_{222}F_9O_{42}S_3Si_{24}$: C 41.40, H 6.58, S 2.83; found: C 42.07, H 6.95, S 2.80; FTIR (KBr): $\tilde{\nu} =$ 2952, 2921, 2870, 1614, 1530, 1509, 1470, 1415, 1366, 1329, 1169, 1080 cm^{-1}.

Characterization

^1H NMR spectra were recorded at room temperature, using residual protonated solvents as internal standards. Elemental analysis was performed on an Elementar Vario El system. UV/Vis spectra were recorded on a Varian Cary model 50 UV/Vis spectrophotometer. Infrared (IR) spectra were obtained on a Bruker Vector 22 spectrometer in the range $\tilde{\nu} = 400$–$4000\ cm^{-1}$ at a resolution of $4\ cm^{-1}$ (128 scans were collected). Samples for thermogravimetry (TG) studies were transferred to open platinum crucibles and analyzed using a TA Instruments model SDT-TG Q 600 system at a heating rate of $5\ ^\circ C\,min^{-1}$. ^{29}Si NMR spectra were measured on a Varian Infinity plus 300 NMR spectrometer from sample solutions in DMF. The repetition time was 60 s. XRD measurements were performed on an X-ray powder diffractometer (BRUKER D8 Focus) employing $Cu_{K\alpha}$ radiation ($\lambda = 1.5418$ Å), operating at 40 kV and 40 mA. Steady-state luminescence spectra and fluorescence lifetimes were measured on an Edinburgh Instruments model FLS920P spectrometer, with a 450 W xenon lamp as the steady-state excitation source, a double-excitation monochromator (1800 lines mm^{-1}), an emission monochromator (600 lines mm^{-1}), and a semiconductor-cooled Hamamatsu model RMP928 photomultiplier tube. The overall luminescence quantum yield was determined by an absolute method on the aforementioned Edinburgh Instruments FLS920P using an integrating sphere (150 mm diameter, $BaSO_4$ coating).

3. Results and Discussion

Thenoyltrifluoroacetone-functionalized POSS (POSS-TTA) was easily obtained by a very simple procedure,[13] which involved reaction of T-heptasiloxane-triol and Si-TTA at reflux for 4.5 h under an inert gas atmosphere. The product was obtained as a viscous liquid after evaporation of the solvent and repeated washing with MeOH. Reaction of POSS-TTA with $EuCl_3{\cdot}6H_2O$ in a 3:1 molar ratio afforded $(POSS\text{-}TTA)_3Eu$ as a novel luminescent organic–inorganic hybrid material, existing as a viscous liquid at room temperature.

The IR spectrum of commercial T-heptasiloxane-triol (Figure 1 a) shows peaks at $\tilde{\nu} = 3000$–2700 and 1480–$1200\ cm^{-1}$, which can be assigned to the stretching and bending modes of the isobutyl moieties. In addition, an intense peak at $\tilde{\nu} = 1110\ cm^{-1}$ can be attributed to asymmetric stretching of Si-

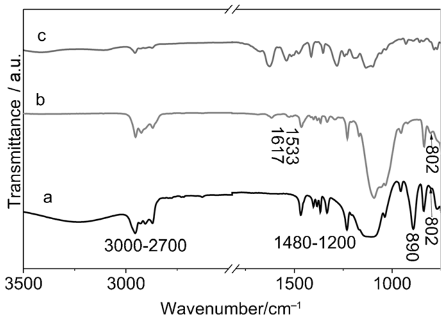


Figure 1. FTIR spectra of a) T-heptasiloxane-triol, b) POSS-TTA, and c) Si-TTA.

O-Si, and the band at $\tilde{\nu}=802\,\text{cm}^{-1}$ can be assigned to Si-C rocking.[67] Two bands at $\tilde{\nu}=3250$ and $890\,\text{cm}^{-1}$ may be assigned to stretching and bending of Si-OH, respectively, which were no longer seen in the IR spectrum of POSS-TTA (Figure 1 b), indicating that the cage was completely condensed.[68] Furthermore, new bands at $\tilde{\nu}=1617$ and $1530\,\text{cm}^{-1}$ are observed in Figure 1 b. By comparison with the IR spectrum of Si-TTA (Figure 1 c), these may be attributed to the C=O and C=C stretching vibrations of TTA moieties from POSS-TTA.[66] The ^{1}H NMR spectrum of POSS-TTA features peaks at $\delta=0.534$ (m, 16H), 0.939 (m, 42H), 1.167 (m, 2H), 1.799 (m, 9H), 2.502 (t, 1H), 3.290 (t, 2H), 7.080 (t, 1H), and 7.634 ppm (d, 2H), confirming the formation of the final product.

The ^{29}Si NMR spectrum of POSS-TTA (Figure 2) features three signals at $\delta=-65.7$, -67.05, and -69.37 ppm, which can be assigned to the Si atom bonded to the diketone group, the Si atoms adjacent to the diketone-substituted Si, and the remaining Si atoms, respectively.[69] The silsesquioxane cage was also investigated by XRD analysis and the XRD pattern of POSS-TTA is shown in Figure 3. Two peaks are observed in the XRD pattern: the sharper one at $2\theta=7.8^\circ$ with a *d*-spacing of 12.95 Å corresponds to the diameter of the POSS-TTA cage, and the much broader peak at $2\theta=19.0^\circ$ with a *d*-spacing of 5.19 Å is due to an amorphous structure arising from a loose molecular packing, which is caused by the substitution of isobutane by the diketone moiety.[70]

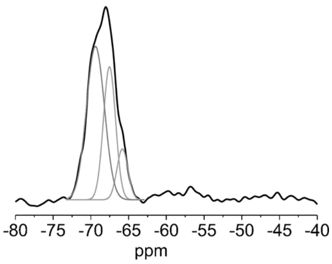


Figure 2. ^{29}Si NMR spectrum of POSS-TTA showing peak deconvolution.

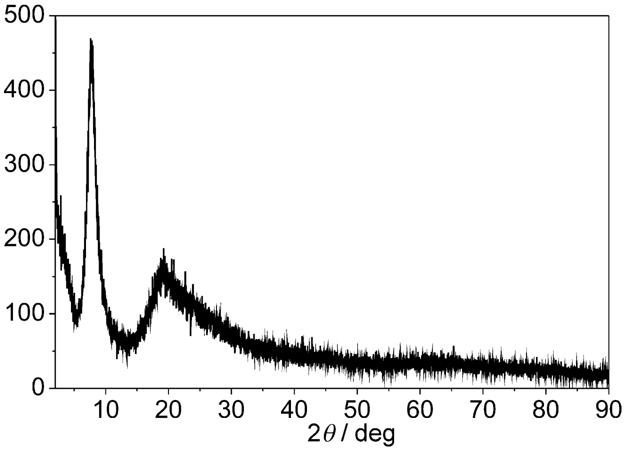


Figure 3. XRD pattern of POSS-TTA.

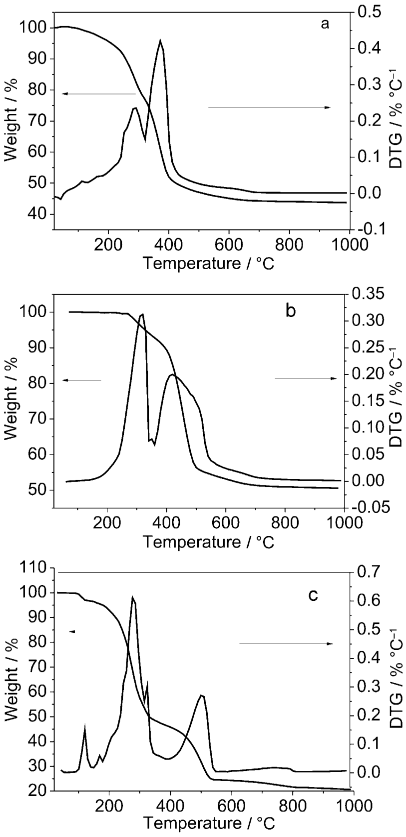


Figure 4. TG and DTA curves of a) POSS-TTA, b) (POSS-TTA)$_3$Eu, and c) [Eu(TTA)$_3$]·2 H$_2$O.

The thermal analysis curve of POSS-TTA is shown in Figure 4 a. A total mass loss of 65.41 % was observed. Decomposition occurred in two main steps. The first step with maximum mass loss rate at around 280 °C can be attributed to the decomposition of TTA moieties. The second step, starting at 300 °C and ending at 610 °C, can be ascribed to decompositions of the isobutyl groups and the Si-O-Si structure of the cage; the maximum mass loss rate for this step is at 370 °C. A horizontal thermal curve was observed above 610 °C, corresponding to a residue yield of 44.23 %, a value in good agreement with that expected for the formation of SiO$_2$ (calcd 44.21 %). The TG curve of the molecular hybrid material (POSS-TTA)$_3$Eu, shown in Figure 4 b, reveals two decomposition stages with maximum mass loss rates at 320 and 420 °C, respectively. No obvious mass loss can be observed before 270 °C, indicating an absence of residual solvent and/or coordinated water molecules in (POSS-TTA)$_3$Eu. In the TG curve of [Eu(TTA)$_3$]·2 H$_2$O (Figure 4 c), three main decomposition stages with maximum mass loss rates at 110, 265, and 500 °C, respectively, can be observed. The first stage (4.2 %) corresponds to the removal of coordinated water molecules, and the second and third stages (75.2 %) can be attributed to decomposition of the TTA ligand (calcd 77 %). A plateau is seen above 800 °C, implying the formation of stable Eu$_2$O$_3$ (21.36 %), which is in good agreement with the calculated amount for [Eu(TTA)$_3$]·2 H$_2$O (21.79 %). Comparison of Figure 4 b with Figure 4 c shows that the thermal stability of (POSS-TTA)$_3$Eu is significantly improved.

The room temperature electronic spectra of POSS-TTA and the corresponding europium(III) complex ((POSS-TTA)$_3$Eu) recorded in EtOH solution are shown in Figure 5. The absorption spectrum of POSS-TTA exhibits a broad band in the region $\lambda = 200–400$ nm, which can be attributed to the singlet-singlet $\pi \rightarrow \pi^*$ enol absorption of the β-diketone moieties, with main components peaking at $\lambda = 240$, 263, and 334 nm. Upon complexation with europium(III), the peak at 334 nm is red-shifted to 343 nm due to the formation of larger conjugated chelate rings.[71]

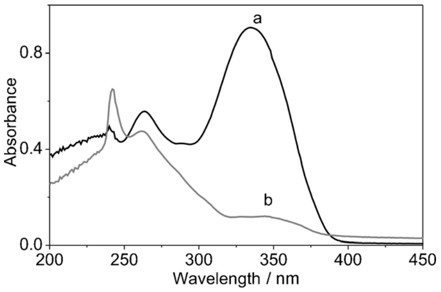


Figure 5. Absorption spectra of a) POSS-TTA and b) (POSS-TTA)$_3$Eu in EtOH at 1×10^{-5} M.

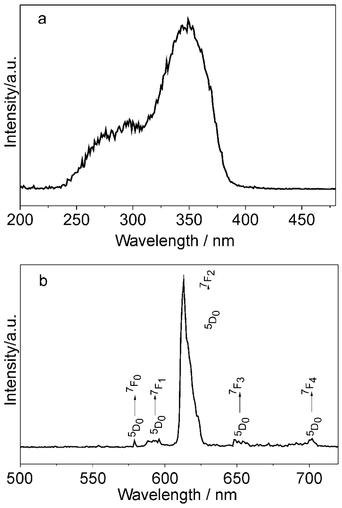
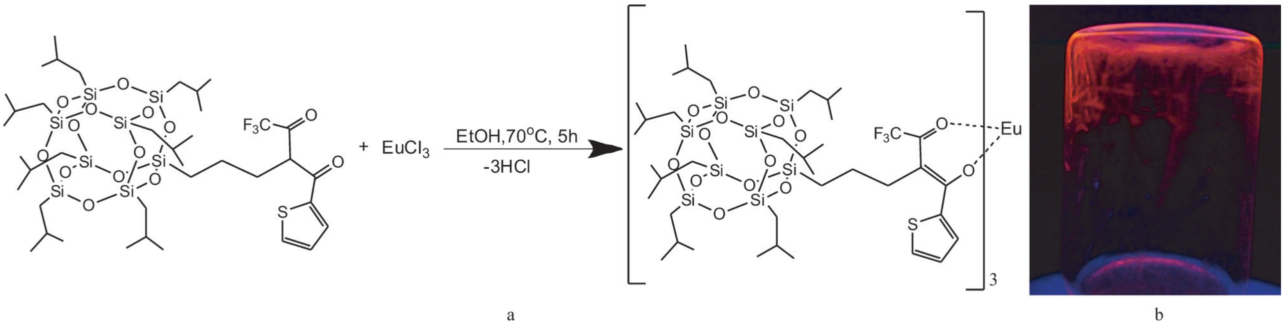


Figure 6. a) Excitation and b) emission spectra of (POSS-TTA)$_3$Eu. The excitation spectrum was obtained by monitoring the $^5D_0 \rightarrow {}^7F_2$ transition at 613 nm; the emission spectrum was obtained at an excitation wavelength of 350 nm.

The excitation and emission spectra of (POSS-TTA)$_3$Eu are shown in Figure 6. The excitation spectrum obtained by monitoring the $^5D_0 \rightarrow {}^7F_2$ transition at 613 nm displays a broad band in the spectral range $\lambda = 200–400$ nm, which can be attributed to the absorption of POSS-TTA. It is largely overlapped with the UV absorption spectrum of POSS-TTA shown in Figure 5 b, indicating the occurrence of energy transfer from POSS-TTA to Eu^{3+} and confirming the formation of a europium(III) β-diketonate complex between POSS-TTA and Eu^{3+} ions (Scheme 2). Excitation of POSS-TTA-Eu at 350 nm gives rise to characteristic metal-centered Eu^{3+} emissions at 580, 592, 613, 650, and 702 nm, which can be assigned to the $^5D_0 \rightarrow {}^7F_J$ ($J = 0–4$) transitions, respectively. The spectrum is dominated by the hypersensitive transition $^5D_0 \rightarrow {}^7F_2$, which is responsible for the red emission color shown in Scheme 2 b, suggesting that the coordination environment of the Eu^{3+} ion is free from an inversion center.[53] The intensity ratio I($^5D_0 \rightarrow {}^7F_2$)/I($^5D_0 \rightarrow {}^7F_1$) was calculated as 16, implying the formation of a europium(III) complex between Eu^{3+} and POSS-TTA since values higher than 10 are expected for such europium(III) β-diketonate complexes.[72] The absolute quantum yield of POSS-TTA-Eu was determined to be 0.12 by using an integrating sphere according to the reported method.[73] The luminescence decay curve of the $^5D_0$ state was found to be mono-exponential (Figure S1), and the $^5D_0$ excited-state lifetime of Eu^{3+} in POSS-TTA-Eu was determined to be 0.558 ms. This is much longer than the lifetime of [Eu(TTA)$_3$]·2 H$_2$O ($\tau = 0.333$ ms, calculated from the mono-exponential decay curve displayed in Figure S2). The increased $^5D_0$ excited-state lifetime of Eu^{3+} in POSS-TTA-Eu compared with that in [Eu(TTA)$_3$]·2 H$_2$O can be rationalized in terms of confinement of the organic ligand TTA around the POSS core and the absence of coordinated water molecules in the POSS-TTA-Eu complex. The good luminescence properties of the liquid material, such as long lifetime and high color purity, together with its good thermal stability and processability, make it highly promising for use in flexible electronic applications.[63]



Scheme 2. a) The chemical structure of (POSS-TTA)$_3$Eu, and b) a digital photograph taken under UV light ($\lambda_{max} = 365$ nm).

4. Conclusion

In summary, a novel thenoyltrifluoroacetone-functionalized POSS, named POSS-TTA, has been synthesized by corner-capping of a commercially available partially condensed trisilanol isobutyl POSS with a silylated thenoyltrifluoroacetone. The obtained POSS-TTA is a viscous liquid at room temperature. Complexation of POSS-TTA with Eu^{3+} ions results in a red-emitting molecular organic–inorganic hybrid liquid material, which shows significantly improved thermal stability compared with $[Eu(TTA)_3]\cdot 2H_2O$. The good luminescence properties of the liquid material, such as long lifetime and high color purity, together with its good thermal stability and processability, make it highly promising for use in next-generation organic devices such as flexible displays. We believe that this work provides an alternative to grafting luminescent lanthanide complexes to silica through Si–C covalent bonds, and expands the field of lanthanide-based luminescent organic–inorganic hybrid materials.

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Keywords: europium(III) β-diketonate complex · hybrid materials · lanthanides · luminescence · POSS · soft materials

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