Photoluminescence of Binary and Ternary Europium-based Polyhedral Oligomeric Silsesquioxane and Sol–Gel Complexes

Pardeshi Hima Bindu,[†] Begari Prem Kumar,[‡] Raghuveer Sherial,[§] Avvaru Praveen Kumar,[¶,*] Bui The Huy,[‖] and Yong-Ill Lee[‖]

[†] *Telangana Tribal Welfare Residential Degree College, Suryapet, Telangana, 508213, India*
[‡] *Research and Development, Tata Steel Limited, Janshedpur, Jharkhand, 831001, India*
[§] *Sai Life Sciences Limited, IKP, Shameerpet, Hyderabad, Telangana, 500078, India*
[¶] *Department of Applied Chemistry, School of Applied Natural Science, Adama Science and Technology University, Adama, Ethiopia. *E-mail: drkumar.kr@gmail.com*
[‖] *Department of Chemistry, Changwon National University, Changwon 641-773, Republic of Korea*

Received April 26, 2020, Accepted July 8, 2020

Keywords: Europium hybrid complexes, Ternary and binary complexes, POSS, Sol–gel method

Development of the organic–inorganic hybrid materials is the interesting nanomaterials of light emitting because of their good chemical, mechanical, and thermal stability.[1] The lanthanide material that possess narrow and weak absorption bands hard to give luminescence by direct excitation.[2] Generally, lanthanide ions, which possess intense and broad absorption bands, are chelated with organic ligands to increase absorption.[3] The intramolecular energy transfer takes place via excited state of ligand to emitting level of lanthanide, which generates metal-centered luminescence, called antenna effect.[4]

The synthesis of luminescence hybrid material by the sol–gel method is a convenient source to set up complexes of luminescent lanthanide and this method can be possible to perform at ambient temperatures but having a disadvantage of less solubility of these lanthanide complexes. This indicates a comparatively low-doped concentration of sol–gel matrix only can be received, apart from this there is a possibility to form cluster which in turn to get poor luminescent material.[5] To solve the drawback of sol–gel material, replace with polyhedral oligomeric silsesquioxane (POSS) moieties to increase the solubility of the lanthanide complexes. In order to get an effective luminescent material, un-reacted europium salt present in the complex can be removed by dissolving in organic solvents.[6]

POSS is a unique modifier to superior materials because it has the stability which acquired by 3D structure.[7] POSS molecules possess a rigid inorganic core which furnishes thermal and photo-stability, high stiffness, the organic groups at the corner provide processability, compatibility as well as excellent solubility as compared to other materials.[8] A number of POSS-based functional nanomaterials, including, light-emitting materials, ionic liquids, liquid crystals, and dental materials[9] have been demonstrated. The reported materials are mono and/or octa-substituted POSS compounds. The POSS moieties that have internalized to other materials like polymers, organic molecules, and so forth might have spectacular influence on their physical and functional properties, such as mechanical and thermal properties.[10,11]

In this work, we have selected *N*-(3-(triethoxysilyl)propyl)-[1,1′-biphenyl]-4-carboxamide (BiPTMS) and biphenyl-POSS (Biph-POSS) as bridging monomers and 1,10-phenanthroline (phen) as a co-ligand to sensitize the luminescence of europium ions. We synthesized new binary and ternary complexes of POSS material (homogeneous material) which are soluble in most of the organic solvents and sol–gel complexes (heterogeneous material) are insoluble in organic solvents. As-synthesized complexes are characterized and the photoluminescence property of POSS hybrid materials (Eu-Bip-Si and Eu-Bip-POSS) and sol–gel material (Eu-Bip-Phe-Si and Eu-Bip-Phe-POSS) are compared and discussed. The europium-based binary and ternary complexes are shown Figure 1.

Results and Discussion

Initially, Biph-POSS (**7**) was prepared by condensation of isobutyl trimethoxysilane in the presence of LiOH to get 1,3,5,7,9,11,14-heptaisobutyl-tricyclo[7,3,3,15,14]heptasiloxane-3,7,11-trisilanol (incompletely condensed product, trisilanol isobutyl-POSS) (**5**). Subsequently, 3-aminopropyltrimethoxysilane was applied to corner capping reaction to get NH_2-POSS (**6**). This NH_2-POSS reacted with [1,1′-biphenyl]-4-carbonyl chloride (Biph) in the presence of pyridine and anhydrous ether as a solvent to form a functional bridge molecule of Biph-POSS (**7**) (Scheme 1) 70% yield. Biph-POSS was characterized by ^{1}H NMR (Figure S1, Supporting Information), where the peaks at δ 8.30 (d, J = 8.33 Hz, 2H, Ar—H), 7.49–7.56 (m, 4H, Ar—H) and 7.26–7.43 (m, 3H, Ar—H) indicate the presence of 1,1′-biphenyl. The peak at 5.98 (bs, 1H) indicate the presence of NH proton. The peak at δ 2.89 (m, 2H, $NHCH_2$) indicate the existence of *N*-attached CH_2 and

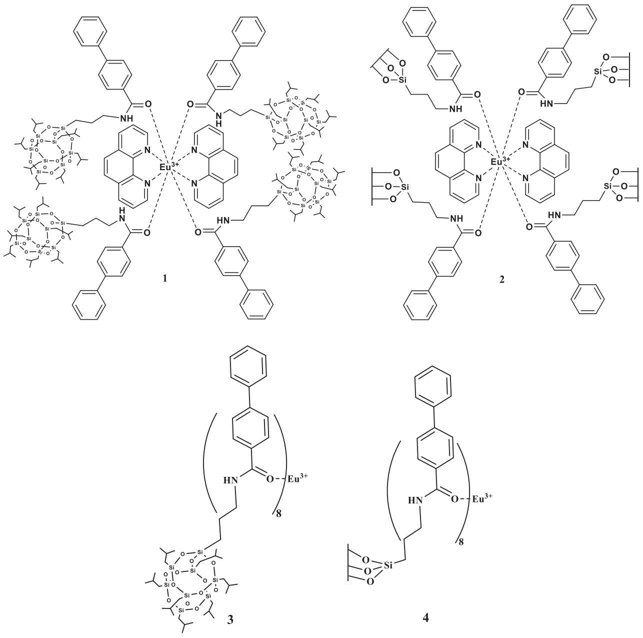
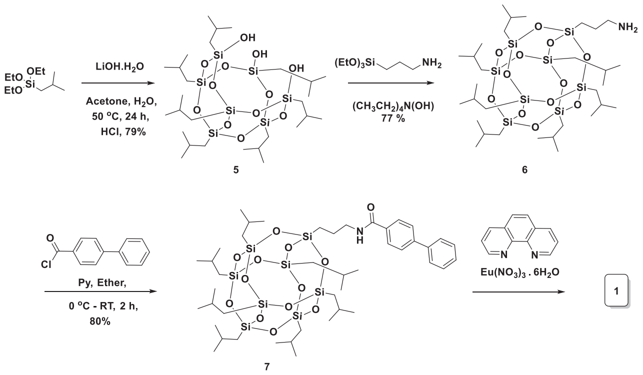


Figure 1. Structures of Eu-Biph-Phe-POSS (**1**), Eu-Biph-Phe-Si (**2**), Eu-Biph-POSS (**3**) and Eu-Biph-Si (**4**) complexes.

peaks at δ 1.58–1.87(m, 9H, N—C—CH_{2-} and C—CH—), 0.72–0.95 (m, 42H, $CH(CH_3)_2$), 0.38–0.68 (m, 18H, CH_2Si) indicate the existence of isobutyl-POSS moieties, which is bridged to [1,1′-biphenyl]-4-carbonyl chloride moiety (Supporting Information Scheme S1). 3-Aminopropyltrimethoxysilane reacts with [1,1′-biphenyl]-4-carbonyl chloride (Biph) in the presence of pyridine to form Biph-Si (**8**) in 70% yield (Scheme 1). This compound was characterized by ^{1}H NMR and ^{13}C-NMR (Supporting Information Figure S2).

Thermogravimetric Analysis

Thermogravimetric curves of Eu-Biph-Phe-POSS, Eu-Biph-Phe-Si, Eu-Biph-POSS, and Eu-Biph-Si complexes are shown in Figure 2. A total mass loss of around 64%, 66%, 58%, and 52% have been noticed for Eu-Biph-Phe-POSS, Eu-Biph-Phe-Si, Eu-Biph-POSS, and Eu-Biph-Si, respectively. The initial loss of weight below 200°C is ascribed to evaporation of residual solvent and physically adsorbed water through partial dehydroxylation. From TGA curves, it has been observed that major weight loss is occurred between 200 and 500°C. This can be assigned to the thermal degradation of organo-silicate framework, which includes cleavage of C—C, C—N and Si—C bonds.[12] The weight loss of Eu-complexes between 350 and 500°C could be due to the decompositions of the SiO_2 residuals and the Si—O—Si structure of the cage. Then, no significant weight loss is occurred when the temperature was above 500°C, which implies the thermal stability of binary and ternary europium-based POSS and sol–gel complexes.



Scheme 1. Synthesis of Eu-Biph-Phe-POSS (**1**)

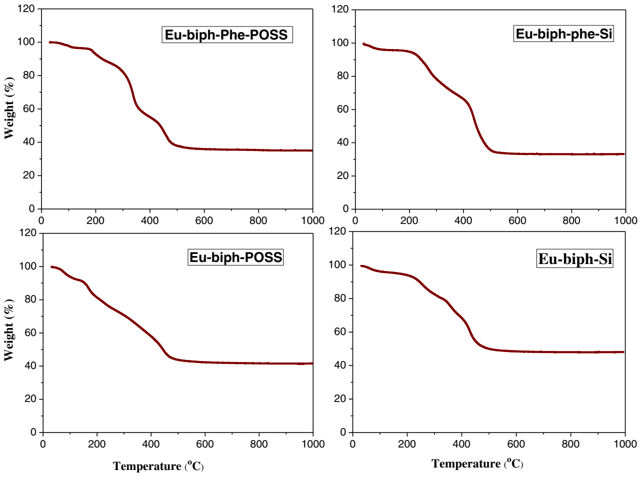


Figure 2. TGA curves of Eu hybrid complexes.

FTIR Analysis

The FTIR of Eu-Biph-Phe-POSS (**1**), Eu-Biph-Phe-Si (**2**), Eu-Biph-POSS (**3**), and Eu-Biph-Si (**4**) are presented in

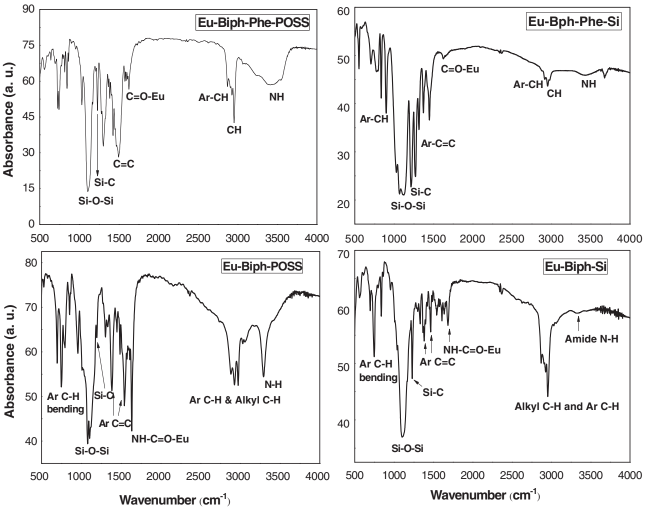


Figure 3. FTIR data of Eu hybrid complexes.

Figure 3. The FTIR spectra of all four complexes showed a bright band at ~1640 cm^{-1} corresponding to ν(Amide—C═O). A stretching vibration at 3300 cm^{-1} was detected for amide ν(N—H), that is supported for the formation of C═O—Eu of europium complex, suggests the involvement of oxygen from amide group in the complexation. The bands from 2879 to 2990 cm^{-1} are mostly because of ν (C—H) stretching vibration on the trident organic arms of POSS. The peaks at 1203, 1195 and 1074, 1078 cm^{-1} belongs to ν(Si—O—Si) and ν(Si—C) stretching vibrations, respectively, which indicate POSS moiety's stability throughout the process.

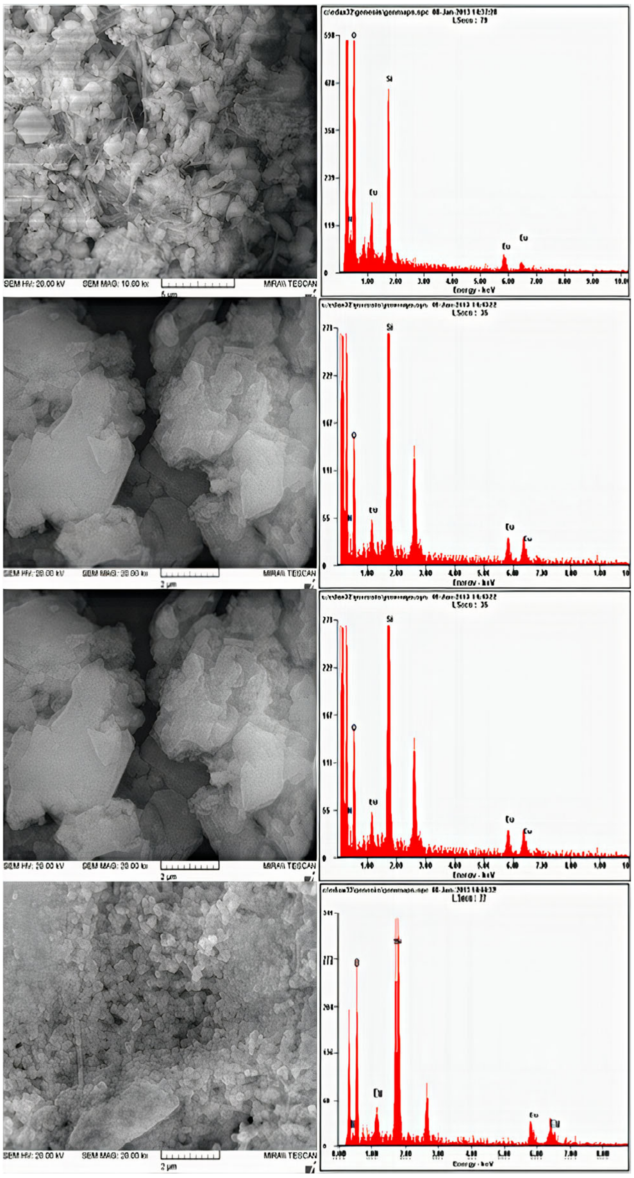


Figure 4. FE-SEM and EDX of Eu hybrid complexes **1**–**4** from top to bottom, respectively.

FE-SEM and EDX Analysis

The surface morphology of europium hybrid complexes was studied by FE-SEM and the microstructural features of the respective Eu-complexes are presented in Figure 4. A clear formation of clumps has been observed in the FE-SEM images and these clumps comprise bigger microstructure. Further, these clumps are dispersed homogenously on the surface of Eu-hydrid powders. These Eu-hydrid complexes are homogeneous molecular-based materials which linked up between organic phase and inorganic phase through strong chemical bonds, which leads to a complexed molecular.[13] EDX experiments were performed to support the europium presence in the all Eu-hybrid complexes. The EDX analyses over the total region of the surface in all the samples clearly affirm the existence of Eu, Si, O, and N elements of Eu-hybrid complexes.

Photoluminescence of Eu-Hybrid Complexes

The luminescent excitation spectrum of Eu-Biph-Phe-POSS and Eu-Biph-Phe-Si samples was recorded at room temperature and monitored at a wavelength of 617 nm and presented in Figure 5. The spectra comprise of broad bands and sharp lines, which attribute to f–f transition of Eu^{3+}. The broad band at 300–375 nm can relate to Si in host absorption band. This band overlapped excitation peaks from $^7F_0 \rightarrow {}^5H_{3\text{-}7}$, $^7F_{0,1} \rightarrow {}^5D_4$ and $^7F_0 \rightarrow {}^5G_{2\text{-}6}$ transitions of Eu^{3+} ions. Figure 5(a) shows f–f transitions of Eu^{3+} ions, which are attributed to $^7F_0 \rightarrow {}^5L_6$ at 397 nm, $^7F_0 \rightarrow {}^5D_3$ at 416 nm and $^7F_0 \rightarrow {}^5D_2$ at 465 nm. In the case of Eu-Biph-POSS and Eu-Biph-Si, the excitation spectra were expanded to short wavelength, as shown in Figure 5 (c) and (d).

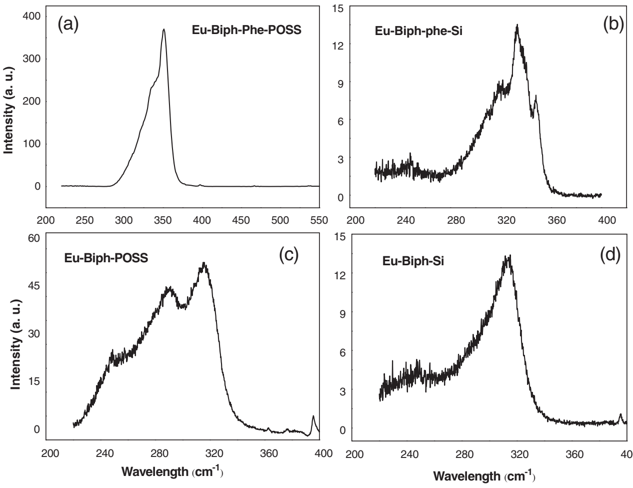


Figure 5. Excitation spectra of (a) Eu-Biph-Phe-POSS, (b) Eu-Biph-Phe-Si, (c) Eu-Biph-POSS and (d) Eu-Biph-Si hybrid complexes.

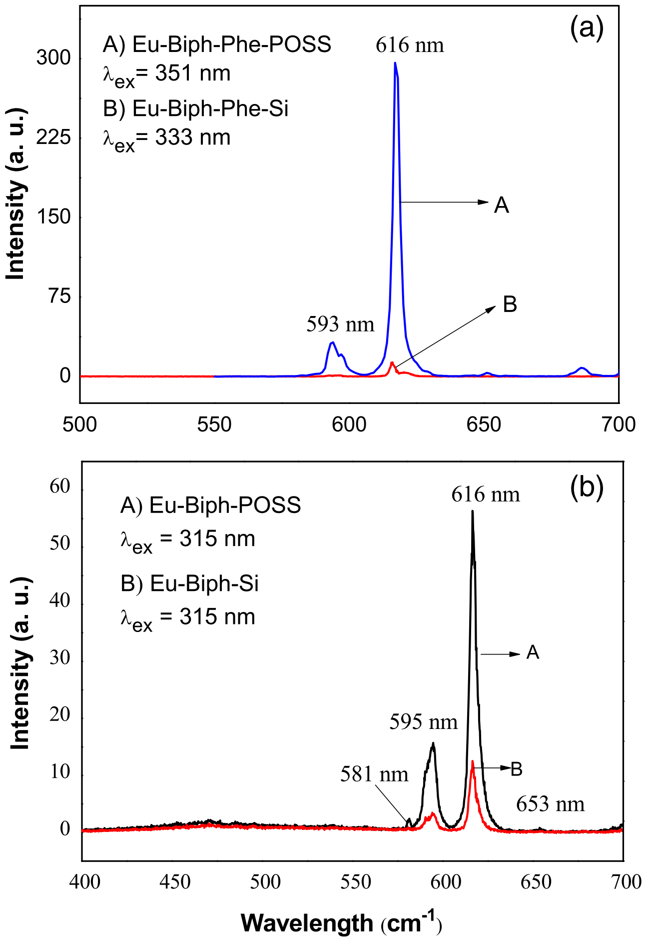


Figure 6. Emission spectra of (a) ternary and (b) binary Eu hybrid complexes.

It is known that photoluminescence spectra of Eu^{3+} ions exhibit emission bands which represented to $^5D_0 \rightarrow {}^7F_J$ (J = 0–6) transitions of Eu^{3+} ions. In this study, the peaks located at 616, 595 and 581 nm related to $^5D_0 \rightarrow {}^7F_2$, $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_0$, respectively (Figure 6(a)). In the case of Eu-Biph-POSS sample, the intensity of peak of 581 nm is very weak (Figure 6(b)) although $^5D_0 \rightarrow {}^7F_0$ is forbidden by the ΔJ selection rules. This observed peak is associated to J-mixing that induced by the perturbation of crystal field. The photoluminescence intensities of Eu-Biph-Phe-POSS and Eu-Biph-POSS samples are stronger than those of Eu-Biph-Phe-Si and Eu-Biph-Si, respectively. The reason can be related to rigid silica cube, nonplanar structure and as a high-performance electrolyte of POSS.[9,14–16]

Experimental

Materials. Tetraethyl orthosilicate (TEOS), isobutyl trimethoxysilane, 1,10-phenanthroline, pyridine, 4-biphenyl carbonyl chloride (BiPh) and $Eu(NO_3)_3.6H_2O$ were purchased from Sigma-Aldrich (St. Louis, MO, USA) and were used without any further purification. The (3-aminopropyl) triethoxysilane was provided by Acros Organics (Fair Lawn, NJ, USA). The solvents and other reagents used in the work were obtained from TCI Chem. Ltd. (Tokyo, Japan).

Methods

Synthesis of Trisilanolisobutyl-POSS (5). Isobutyl trimethoxysilane (1 eq) was dissolved in acetone (4 vol), to this added distilled water (0.80 eq) and lithium hydroxide monohydrate (0.45 eq.) and refluxed for 20 h with vigorous stirring. The resulting solution was acidified with 1 M HCl (4 vol) and a solid precipitated out during addition. Filtered the solid, washed with acetonitrile (5 vol), suck dried for 30 min and then dried under vacuum at 45°C for 4 h to give 74% yield.

Proton NMR in $CDCl_3$ with 400 MHz of **5**: δ 0.64–0.54 (m, 14H, $-CH_2-$), 0.98–0.92 (m, 42H, $(CH_3)_2$), 1.91–1.78 (m, 7H, —CH—) and 6.66 (bs, 3H, OH).

Synthesis of NH_2-POSS (6). Added 3-aminopropyl trimethoxysilane (1 eq) and tetraethyl ammonium hydroxide (20% methanol solution) to a solution of trisilanolisobutyl-POSS (1 eq) in ethanol (6 vol) and stirred the reaction mass for 36 h at 20°C. The solvent (ethanol) was evaporated from the resultant solution to get a solid. This solid was washed with acetonitrile (5 vol), suck dried for 30 min and then dried under vacuum at 45°C 30 min and then dry under vacuum at 45°C to obtain 77% yield as a white solid (Scheme 1).

Proton NMR in $CDCl_3$ with 400 MHz of **6**: δ 0.6 (t, $SiCH_2$, 16H), 0.9 (d, $CH(CH_3)_2$, 42H), 1.7–1.9 (m, CH_2CH, CH_2CH_2, 7H) and 2.6 (t, CH_2NH_2,2H).

Synthesis of BiPh-POSS (7). Dissolved BiPh (1 eq) in 5 vol. of dry ether under N_2 atmosphere. Heptaisobutyloctasiloxane propylamine (NH_2-POSS) (1 eq) and pyridine (4 eq) were dissolved in 4 vol. of ether and added drop wise to the BiPh solution while stirring. The reaction mass was stirred for 4 h at room temperature under N_2 atmosphere. After completion of the reaction, the pyridine hydrochloride salt was filtered. The filtrate was evaporated under vacuum at 45°C to get white solid in 70% yield (Scheme 1).

Proton NMR in $CDCl_3$ with 400 MHz of **7**: δ 8.29 (d, J = 7.5 Hz, 2H, Ar—H), 7.95 (t, J = 7.5 Hz, 1H, Ar—H), 3.34–3.49 (m, 4H, $NHCH_2$), 2.86 (bs, 2H, NH), 1.56–1.89 (m, 21H, $CH_2CH_2CH_2$), 0.81–0.93 (m, 84H, $CH(CH_3)_2$), 0.48–0.56 (m, 36H, CH_2Si).

Carbon-13 NMR ($CDCl_3$): δ 167.2 (Amide), 144.6 (Aromatic), 140.4 (Aromatic), 133.5 (Aromatic), 130.3 (Aromatic), 128.8 (Aromatic), 127.8 (Aromatic), 127.2 (Aromatic), 126.8 (Aromatic), 42.3 (N—$\underline{C}$—), 29.7 ((—$\underline{C}$—Si), 25.6 ($\underline{C}H_3$), 23.8 (—$\underline{C}$—Si), 23 (N—CH_2—$\underline{C}$—), 22.4 ($\underline{C}(CH_3)$.

Synthesis of the Ternary Hybrid Material Eu-Biph-Phe-POSS (1). Dissolved 1,10-phenanthroline (2 eq) and BiPh-POSS (4 eq) in 5 vol. of absolute ethanol while stirring. Added solid $Eu(NO_3)_3.6H_2O$ (1 eq) to the above solution.

Stirred the solution for 24 h and evaporated the solvent by vacuum rotary vapor to get a white solid (Scheme 1). To confirm the reaction, white solid was checked under UV-lamp to get red emitting light.

Synthesis of *N*-(3-(triethoxysilyl) propyl)-[1,1'-biphenyl]-4-carboxamide (8). Dissolved BiPh (1 eq) in 5 vol. of ether under N_2 atmosphere and added drop wise to a solution of amino propylsilane (1 eq) and pyridine (4 eq) in 4 vol. of ether. The reaction mass was stirred for 4 h at room temperature under N_2 atmosphere. The reaction mass was filtered to remove pyridine hydrochloride salt after completion of the reaction. The filtrate was concentrated under vacuum rotary evaporator to get a crude mass. Then the product was purified by column chromatography to yield a white solid of 70% yield (Supporting Information Scheme S1).

Proton NMR ($CDCl_{3,}$ 400 MHz) of **8**: δ 7.86 (dd, J = 8.5, 7.0 Hz, 4H, Ar—H), 7.47 (t, J = 7.3, 7.5 Hz 2H, Ar—H), 7.39 (t, J = 7.3 Hz, 1H, Ar—H), 6.56 (bs, 1H), 3.84 (q, J = 7.0, 6.8 Hz, 6H), 3.50 (q, J = 6.5, 6.0 Hz, 2H), 1.79 (p, 7.07, 13.89 Hz, 2H), 1.23 (t, J = 7.0 Hz, 9H) and 0.74 (t, J = 8.0, 2H).

^{13}CNMR ($CDCl_3$): δ 167.1 (Amide), 144 (Aromatic), 140.1 (Aromatic), 133.58 (Aromatic), 128.9 (Aromatic), 127.94 (Aromatic), 127.41 (Aromatic), 127.2 (Aromatic), 127.17 (Aromatic), 58.5 (O-CH_2-), 42.2 (CH_2-N), 22.9 (CH_2), 18.3 (CH_3(OEt)), 7.84 (CH_2(Si)).

Synthesis of Sol–Gel-based Hybrid Eu-Biph-Phe-Si (2). Dissolved BiPh-Si (4 eq) and 1,10-phenanthroline (2 eq) in 5 vol. of absolute ethanol while stirring. To this solution added $Eu(NO_3)_3.6H_2O$ (1 eq) and continued stirring for 2 h. Then added drop wise a mixture of tetraethyl orthosilane and deionized water, followed by the addition of one drop of dilute HCl to promote hydrolysis. The mixture was then transferred to RB flask and kept for reflux at 65°C for 3 days. The obtained gels were denoted as Eu-BiP-Si (Supporting Information Scheme S1).

Synthesis of Binary Hybrid Material Eu-Biph-POSS (3). Dissolved BiPh-POSS (**7**) (6 eq.) in 2 mL of absolute ethanol while stirring and added 1 eq. of $Eu(NO_3)_3.6H_2O$. After 24 h of stirring, evaporated the solvent under vacuum rotary vapor to obtain a solid in white color (Supporting Information Scheme S2). To confirm the reaction, white solid was checked under UV-lamp to get red emitting light.

Synthesis of Sol–Gel-based Hybrid Eu-Biph-Si (4). Dissolved (1 eq) of biphenyl propyltriethoxysilane in 5 vol. of dry ethanol along with stirring. Added approximately one-third amount of $Eu(NO_3)_3.6H_2O$ to the solution. Then added tetraethyl orthosilicate and deionized water drop wise. After 2 h of stirring, added one drop of dilute HCl to promote hydrolysis. The mixture was then transferred to a RB flask and kept for reflux at 60°C for 16 h. The obtained gels were denoted as Eu-BiP-Si (Supporting Information Scheme S3).

Characterization Techniques. FTIR (6300 Spectrometer, JASCO, Japan) analysis was carried out in the range of 400–4000 cm^{-1} using a resolution of 0.07 cm^{-1}. The pellet method was used to prepare the samples. The spectrum was recorded with an average of 10 scans. The nuclear magnetic resonance (NMR) study for all synthesized samples was performed by NMR spectrometer (Avance 400; Bruker, Germany) using $CDCl_3$ as a solvent. Field-emission scanning electron microscope (FE-SEM, MIRA II, TESCON, Czech) was executed to see the surface morphology of the samples. The elemental analysis was carried out using energy dispersive X-ray analysis (EDXA; Oxford, USA) to support the europium presence in the samples. Thermogravimetric analysis (TGA) experiments were performed using a SDT Q200 (USA) instrument under a flow of nitrogen gas. A Shimadzu, Japan photoluminescence spectrophotometer (RF-5301) was used to examine the excitation and emission characteristics of the europium complexes.

Acknowledgments. Publication cost of this paper was supported by the Korean Chemical Society.

Supporting Information. Additional supporting information may be found online in the Supporting Information section at the end of the article.

References

1. J. Wen, G. L. Wilkes, *Chem. Mater.* **1996**, *8*, 1667.
2. J.-C. G. Bünzli, *Chem. Rev.* **2010**, *110*, 2729.
3. D. A. Wilkinson, J. E. Watkin, *Forensic Sci. Int.* **1993**, *60*, 67.
4. Y. Hasegawa, Y. Kitagawa, T. Nakanishi, *NPG Asia Mater.* **2018**, *10*, 52.
5. K. Binnemans, P. Lenaerts, K. Driesen, C. Görller-Walrand, *J. Mater. Chem.* **2004**, *14*, 191.
6. B. Prem Kumar, B. V. D. Vijay Kumar, C. M. Raghavan, S. J. Harshavardhan, S.-S. Yi, S. Gandhi, J. Z. Jiang, K. Jang, D.-S. Shin, *J. Mater. Sci.* **2013**, *48*, 7533.
7. H. Zhou, Q. Ye, J. W. Xu, *Mater. Chem. Front.* **2017**, *1*, 212.
8. J. L. Zhou, Y. C. Zhao, K. C. Yu, X. P. Zhou, X. L. Xie, *New J. Chem.* **2011**, *35*, 2781.
9. K. Tanaka, F. Ishiguro, Y. J. Chujo, *Am. Chem. Soc.* **2010**, *132*, 17649.
10. H. Y. Xu, S.-W. Kuo, J.-S. Lee, F.-C. Chang, *Macromolecules* **2002**, *35*, 8788.
11. S. Gandhi, B. Prem Kumar, K. Thandavan, K. Jang, D.-S. Shin, A. Vinu, *New J. Chem.* **2014**, *38*, 2766.
12. P. Tien, L. K. Chau, *Chem. Mater.* **1999**, *11*, 2141.
13. H. J. Zhang, B. Yan, S. B. Wang, J. Z. Ni, *J. Photochem. Photobiol. A Chem.* **1997**, *109*, 223.
14. K. Tanaka, F. Ishiguro, J. Jong-Hwan, H. Tatsuhiro, Y. Chujo, *NPG Asia Mater.* **2015**, *7*, e174.
15. W. Fuke, L. Xuehong, H. Chaobin, *J. Mater. Chem.* **2011**, *21*, 2775.
16. D. Beata, Ż. Patrycja, M. Bogdan, *Polymers* **2019**, *11*, 504.