

Luminescent Triazine-Containing Bridged Polysilsesquioxanes Activated by Lanthanide Ions

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Luminescent lanthanide-complex-bridged polysilsesquioxanes were prepared by sol–gel processing of a monomer with a large heterocyclic bridging group in the presence of lanthanide ions under acidic conditions. SEM, XRD, FTIR, luminescence spectra and luminescence decay analysis were used to characterize the obtained materials. The 5D_0 quantum effi-

ciency and the number of the water molecules coordinated to the Eu^{3+} ion were theoretically estimated on the basis of emission spectra and the lifetime of the 5D_0 state.

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Introduction

Bridged polysilsesquioxanes are hybrid organic–inorganic materials derived from the sol–gel processing of monomers containing a variable organic bridging group and two or more trialkoxysilyl groups.^[1–4] The organic group, covalently bonded to the trialkoxysilyl groups, can be varied in composition, length, rigidity, and functionalization. Thus, the properties of the resulting hybrid solids can be tuned by the introduction of appropriate organic functionality into the silicate network through covalent linkage. The easy preparation of these materials, that is, a “one-pot” synthesis, is another tremendous advantage. Bridged silsesquioxanes have proven to be efficient candidates for applications in optical devices,^[5–8] high-capacity absorbents,^[9–11] 3D information storage media,^[12] and proton-conducting media for fuel cells.^[13,14]

To date, great effort has been directed to optical applications of bridged polysilsesquioxanes by incorporating various chromospheres in the bridging groups.^[15–18] The use of dye molecules as bridging groups offers a high loading of chromospheres and avoids the leaching or phase separation of the dye molecule. However, there are relatively few studies on the preparation of luminescent polysilsesquioxanes with lanthanide complexes as the bridging group.^[19–23] Lanthanide complexes are well-known molecular luminescent materials, which are characterized by characteristic narrow emission bands and long radiative lifetimes of the excited

state. These properties are favorable for a broad range of applications such as fiber amplifiers and solid-state lasers.^[24,25] Thus, it would be an interesting topic to develop bridged polysilsesquioxanes containing lanthanide compounds from the viewpoints of academic interest and practical applications. In this contribution, we present a novel urea-based tris(silylated) monomer containing large organic bridging groups of complex chemical structure, consisting of a heterocyclic ring (triazine) integrated through flexible alkyl chains with three triethoxysilyl groups. The synthesis and characterization of the triazine-bridging monomer derived from melamine are described; the derived multifunctional monomer was afterward submitted to complexation with Ln^{3+} ions and to a sol–gel process in order to obtain the luminescent bridged polysilsesquioxanes. The aims of the present work are to (i) enrich the family of bridged polysilsesquioxane by incorporation of triazine into the bridging group and (ii) investigate the sensitization of Ln^{3+} ions by the bridged polysilsesquioxanes.

Results and Discussion

Hydrolysis and condensation of monomers containing a variable organic bridging group with two or more trifunctional silyl groups under different conditions can lead to bridged polysilsesquioxanes. For example, trifunctional arylsilanes preferentially form as oligosilsesquioxanes rather than gels. At high monomer concentrations, however, gels can be prepared from trifunctional derivatives by heating in the presence of a strong base. In this work, the luminescent bridged polysilsesquioxanes were obtained by hydrolysis and condensation of the urea-based tris(silylated) monomer containing large organic bridging groups under acidic conditions.^[26]

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Supporting information for this article is available on the WWW under <http://www.eurjic.org> or from the author.

The FTIR spectra of the monomer and the monomer with Eu^{3+} ($\text{Eu}^{3+}/\text{monomer ratio} = 0.5$) are shown in Figure 1. For the monomer, the $\nu(\text{Si}-\text{C})$ and $\nu(\text{Si}-\text{OEt})$ absorption bands characteristic of trialkoxysilyl functions appear at 1194 and 1080 cm^{-1} , respectively. The sharp bands located at 1697 and 1534 cm^{-1} corresponding to the urea $\text{NH}-\text{CO}-\text{NH}$ function provide strong evidence that the reaction between melamine and 3-(triethoxysilyl)propyl isocyanate was successful. Furthermore, the characteristic bands of melamine at 1616, 1480, 1360, and 816 cm^{-1} are also observed.^[27] Upon addition of Eu^{3+} ions to the monomer, the $\nu(\text{C}=\text{O})$ vibration is shifted to lower frequency ($\Delta\nu = 22 \text{ cm}^{-1}$); this could be ascribed to the complexation of the Eu^{3+} ions with the oxygen atom of the carbonyl group. It is well established that complexation of the metallic ion with the oxygen atom of the carbonyl group can induce the $\nu(\text{C}=\text{O})$ vibrations to shift lower frequencies ($\Delta\nu = 20\text{--}40 \text{ cm}^{-1}$).^[21] Sol-gel processing of the monomer led to bridged polysilsesquioxanes, which were also characterized by infrared spectroscopy (Figure 2). In both cases, the $\nu(\text{Si}-\text{C})$ vibration located in the 1194 cm^{-1} range is observed in the IR spectra of the hybrid materials, and this is consistent with the fact that no great ($\text{Si}-\text{C}$) bond cleavage occurs during hydrolysis/condensation reactions. The broad absorption band at 1120–1000 cm^{-1} [$\nu(\text{Si}-\text{O}-\text{Si})$] indicates the formation of siloxane bonds, and residual silanol groups are evidenced by the $\nu(\text{Si}-\text{OH})$ stretching vibration at 916 cm^{-1} . Complexation of Ln^{3+} ions by the bridging organic group in the bridged polysilsesquioxane matrices can be clearly evidenced by infrared spectroscopy. The $\nu(\text{C}=\text{O})$ vibration is shifted to low frequency after complexation of the carbonyl group.

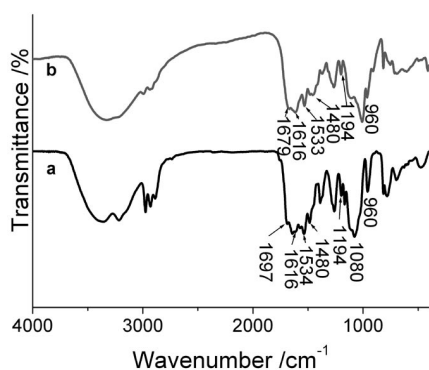


Figure 1. FTIR spectra of (a) the monomer and (b) the monomer with Eu^{3+} ($\text{Eu}^{3+}/\text{monomer ratio} = 0.5$).

X-ray powder diffraction analysis of the solids allowed information about the nanometer scale organization to be obtained. The X-ray powder diffraction diagrams of MICPTES-Hb and MICPTES-Hb-Eu are given in Figure 3. In both cases, two broad patterns at medium scattering angle ($2\theta = 5\text{--}50^\circ$) exhibit two resolved Bragg diffraction peaks for MICPTES-Hb at $2\theta = 21.16$ and 9.46° and for MICPTES-Hb-Eu at $2\theta = 21.63$ and 10.51° , respectively. For both cases, the broad pattern observed at ca. 21° can be attributed to the $\text{Si}-\text{O}-\text{Si}$ contribution, as observed

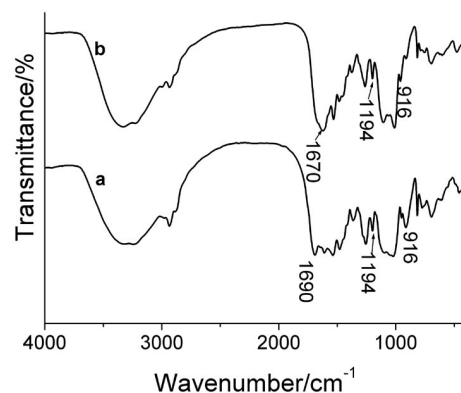


Figure 2. FTIR spectra of (a) MICPTES-Hb and (b) MICPTES-Hb-Eu.

in other nanostructured hybrid materials by comparison with SiO_2 xerogels.^[28] The pattern displayed at ca. $9\text{--}11^\circ$ may be attributed to a periodic arrangement of the monomer during the sol-gel processing.^[29] The addition of Eu^{3+} ions can affect the periodicity structure of the materials, as evidenced by the decreased d value (from 9.2 to 7.9 $\text{\AA}$) of the first XRD pattern as indicated by the arrow in Figure 3.

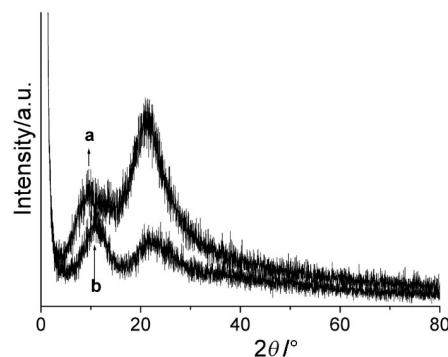


Figure 3. XRD diagrams of (a) MICPTES-Hb and (b) MICPTES-Hb-Eu.

Figure 4 shows the SEM images of MICPTES-Hb and MICPTES-Hb-Eu. The uniform frameworks on the surfaces suggest that homogeneous, molecular-based materials were obtained.^[30] The SEM images of both samples revealed a large particle morphology (ca. $5\text{--}10 \mu\text{m}$ long) with various sizes and shapes.

In order to investigate the sensitization of lanthanide ions by the bridged polysilsesquioxane, the emission spectrum of the bridged polysilsesquioxane MICPTES-Hb was studied, which was obtained by excitation at 335 nm (see the Supporting Information). The photoluminescence spectra show the presence of two main contributions of a band centered at 410 nm and another band with a peak at 465 nm.

The bridged polysilsesquioxane MICPTES-Hb-Eu shows red photoluminescence upon radiation with ultraviolet light ($\lambda = 365 \text{ nm}$). The excitation and emission spectra are shown in Figure 5. The excitation spectrum was monitored around the more-intense line of the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transi-

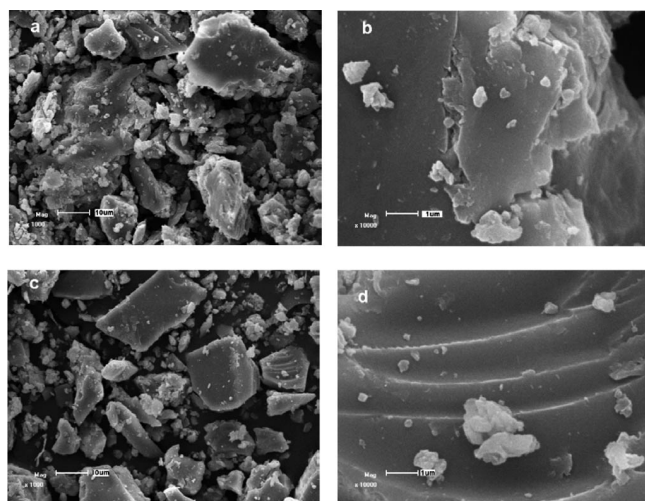


Figure 4. SEM images of materials (a, b) MICPTES-Hb and (c, d) MICPTES-Hb-Eu.

tion at 612 nm. A large broad band between 250 and 450 nm with two main components peaking at ca. 275 and 335 nm, respectively, overlapped with relatively low-intensity peaks ascribed to an intra- $4f^6$ line can be observed. The band at 275 nm can be attributed to $\pi-\pi^*$ transition based on the conjugated double bonds of the heterocyclic ligand, and the band at 335 nm is assigned to the conjugated system between the heterocyclic and urea bonds.^[19] Moreover, the lower relative intensity of the Eu^{3+} ion strongly suggests that the metal ions are essentially excited by a sensitized process rather than by direct population of the intra- $4f^6$ levels. The luminescence spectrum was measured with 335 nm as the excitation wavelength. The narrow peaks observed in the spectrum are transitions between the $^5\text{D}_0$ excited state and the different J levels of the ground term $^7\text{F}_J$ ($J = 0-4$). The presence of the forbidden $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition indicates that Eu^{3+} ions are located in a coordination sphere with low symmetry.^[31] The $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition corresponds to a parity-allowed magnetic dipole transition, which is just about independent of the host material.^[32] The hypersensitive $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition varies strongly with the local surrounding around the Eu^{3+} ions. Its intensity increases when the lattice environment is distorted and contains certain components of noninversion symmetry.^[31] Thus, the ratio (R) between the intensities of the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ and $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transitions can be considered as a parameter to probe the “asymmetry” of the Eu^{3+} sites. Here, the R value is about 4, indicating that the local surrounding observed in our sample is highly asymmetric. Furthermore, the fine splitting of the transition lines is related to a “crystalline” lanthanide ion environment rather than an amorphous one,^[33] suggesting coordination between the Eu^{3+} ion and the oxygen atoms of the carbonyl group as well as the nitrogen atoms from the melamine unit as shown in Scheme 1. The luminescence decay curve of MICPTES-Hb-Eu was recorded with an emission at 612 nm. The fluorescence decay profile is single exponential (Figure 6), revealing a lifetime value around 0.744 ± 0.003 ms.

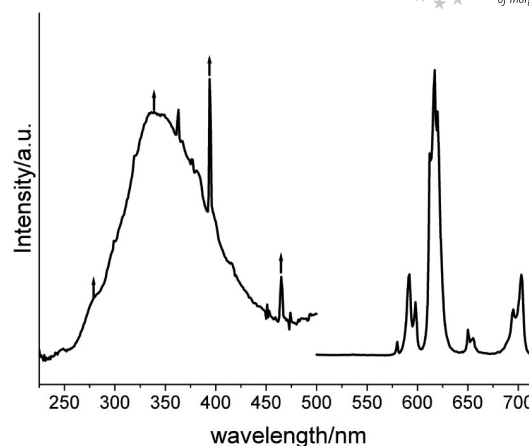
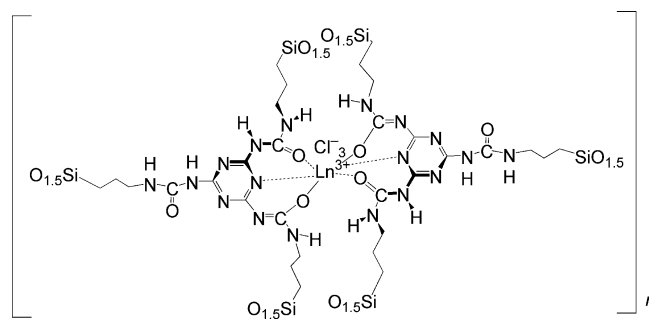


Figure 5. Excitation (left) and emission (right) spectrum of MICPTES-Hb-Eu.



Scheme 1. Predicted structure of the bridged polysilsesquioxane MICPTES-Hb-Ln.

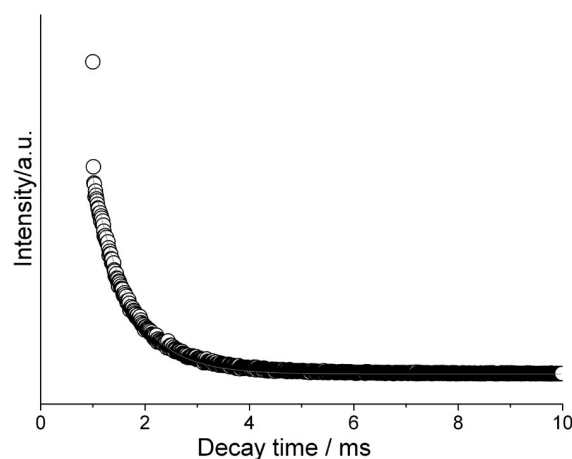


Figure 6. Decay curve of MICPTES-Hb-Eu.

The $^5\text{D}_0$ quantum efficiency (q) and the number of the water molecules coordinated to the Eu^{3+} ion can be estimated on the basis of the emission spectrum and the lifetime of the $^5\text{D}_0$ state by using the following equations according to ref.^[34] By assuming that only nonradiative and radiative processes are involved in the depopulation of the $^5\text{D}_0$ state, q may be defined by Equation (1).

$$q = \frac{k_r}{k_r + k_{nr}} \quad (1)$$

where k_r and k_{nr} are the radiative and nonradiative probabilities, respectively. The radiative contribution may be calculated from the relative intensities of the $^5D_0 \rightarrow ^7F_J$ ($J = 0-4$) transitions and can be expressed by Equation (2).

$$k_r = \frac{A_{0-1}E_{0-1}}{S_{0-1}} \sum_{J=0}^4 \frac{S_{0-J}}{E_{0-J}} \quad (2)$$

where A_{0-1} is Einstein's coefficient of spontaneous emission between the 5D_0 and 7F_1 level, usually considered to be equal to 50 s^{-1} , and E_{0-J} and S_{0-J} are the energy and the integrated intensity of the $^5D_0 \rightarrow ^7F_J$ transitions, respectively.

The number of water molecules (n_w) coordinated to the Eu^{3+} ions in the bridged polysilsesquioxanes can be estimated by modification of Horrock's equation,^[35] and it is given in Equation (3).

$$n_w = 1.1(k_{\text{exp}} - k_r - 0.31) \quad (3)$$

where k_{exp} is the reciprocal value of the 5D_0 lifetime. The data obtained are summarized in Table 1.

Table 1. Experimental 5D_0 lifetime, calculated radiative and nonradiative 5D_0 decay rate, 5D_0 quantum efficiency value, and the number of water molecules coordinated to the Eu^{3+} ions.

Sample	τ / ms	k_r / ms^{-1}	k_{nr} / ms^{-1}	$q / \%$	n_w
MICPTES-Hb-Eu	0.744	0.404	0.94	30	0.6

The relatively longer lifetime and lower number of coordinated water molecules relative to the published data^[19] show that the Eu^{3+} ions are well protected from the environment. It is well established that the chelating moieties are in their enolized form.^[36] Thus, it is reasonable to predict the structure (Scheme 1) of the obtained bridged polysilsesquioxanes.

The europium(III) ion can be replaced in this system by terbium(III) ions. The obtained material, MICPTES-Hb-Tb, shows strong green photoluminescence when irradiated under a UV lamp. The excitation spectrum was monitored at 544 nm, and it is similar to that of MICPTES-Hb-Eu, that is, a large broad band with two main components peaking at ca. 275 and 335 nm are observed (Figure 7). Nevertheless, no f-f transition could be detected. This means that very effective energy transfer from the hybrid materials to the terbium(III) ions occurs. The luminescence spectrum was measured with 335 nm as the excitation wavelength. The emission spectrum of MICPTES-Hb-Tb obtained by excitation at 335 nm presents four emissions lines for the Tb^{3+} ions, peaking at 489 ($^5D_4 \rightarrow ^7F_6$), 545 ($^5D_4 \rightarrow ^7F_5$), 586 ($^5D_4 \rightarrow ^7F_4$), and 620 nm ($^5D_4 \rightarrow ^7F_3$). The $^5D_4 \rightarrow ^7F_5$ green emission is the most prominent peak, and no emission arising from the host material can be detected, suggesting efficient energy transfer from the host material to the Tb^{3+} ions. The luminescence decay of the 5D_0 level can be well fitted by one exponential as evidenced in Figure 8. The fitted value for the lifetime is $1.31 \pm 0.006 \text{ ms}$.

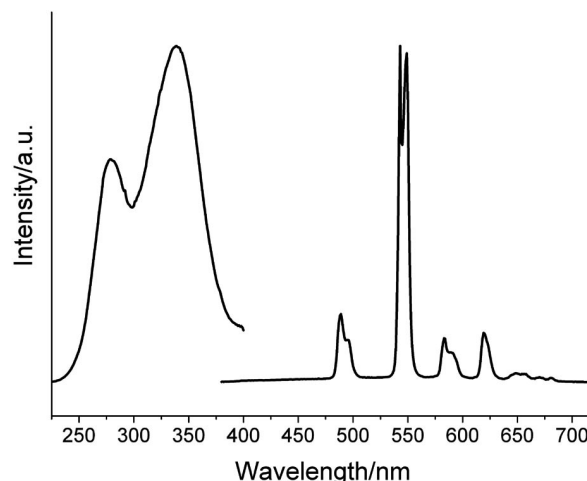


Figure 7. Excitation (left) and emission (right) spectra of MICPTES-Hb-Tb.

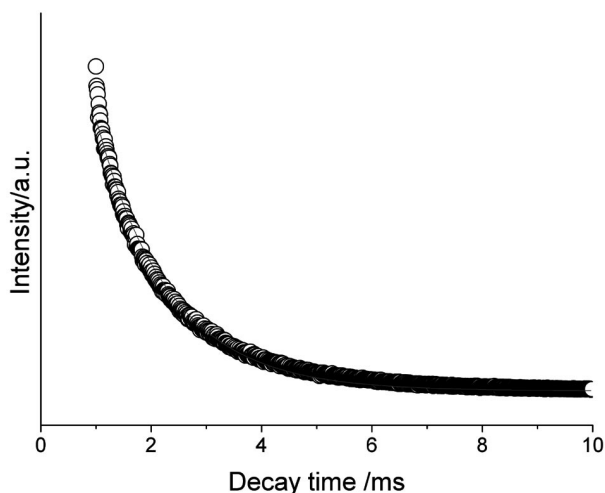


Figure 8. Decay curve of MICPTES-Hb-Tb.

Conclusions

In summary, we synthesized a monomer containing large organic bridging groups of complex chemical structure, consisting of a heterocyclic ring integrated through flexible alkyl chains with three trimethoxysilyl groups. Luminescent bridged polysilsesquioxanes possessing the luminescence characteristics of Eu^{3+} and Tb^{3+} ions were obtained by hydrolysis and condensation of the new monomer in the presence of Eu^{3+} and Tb^{3+} ions, respectively. The predicted structure of the materials was given based on FTIR analysis, luminescence spectra, and data from the literature.

Experimental Section

Materials: Melamine (Acros) and 3-(triethoxysilyl)propyl isocyanate (Aldrich) were used as received. $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$ were obtained by dissolving Eu_2O_3 and Tb_4O_7 into HCl solution. (37.5%).

Preparation of Monomer: To a solution of melamine (1 mmol) dissolved in DMSO (5 mL) was added 3-(triethoxysilyl)propyl isocyanate (0.75 mL, 3 mmol), and the mixture was heated at reflux at 120 °C for 5 h. The solution turned yellow, and the mixture was cooled to room temperature followed by reduced pressure distillation to remove DMSO. Upon the addition of a large excess of ether, a white precipitate formed that was filtered, washed with hexane, and vacuum dried. ^1H NMR ($[\text{D}_6]\text{DMSO}$): δ = 6.70 (s, 3 H, NH), 5.81 (br. s, 3 H, NH), 3.75 (q, 18 H, OCH_2), 3.31 (t, 6 H, NCH_2), 1.54 (quint., 6 H, CH_2), 1.16 [t, 27 H, $\text{CH}_3(\text{OEt})$], 0.54 (t, 6 H, SiCH_2) ppm.

Preparation of MICPTES-Hb: To a solution of the monomer (1 mmol) dissolved in DMSO (5 mL) was dropwise added ethanol (7.5 mL) and a solution of HCl (0.2 M, 1.25 mL). The mixture was heated at 60 °C for 12 h, and the mixture was then concentrated to 30% of its original volume. The solution was then poured into a flat-bottomed plastic box and dried at 80 °C for 4 d. The transparent orange monolith was obtained.

Preparation of MICPTES-Hb-Ln: To a solution of the monomer (1 mmol) dissolved in DMSO (5 mL) was dropwise added a solution of LnCl_3 ($\text{Ln} = \text{Eu}, \text{Tb}$, 0.5 mmol) in ethanol (7.5 mL) and a solution of HCl (0.2 M, 1.25 mL). The mixture was heated at 60 °C for 12 h, and the mixture was then concentrated to 30% of its original size. The solution was then poured into a flat-bottomed plastic box and dried at 80 °C for 4 d. The transparent orange monolith was obtained. It is named as MICPTES-Hb-Eu and MICPTES-Hb-Tb for Eu^{3+} and Tb^{3+} ions, respectively.

Characterization: Infrared (IR) spectra were obtained with a Bruker Vector 22 spectrometer by using KBr pellets for solid samples from 400–4000 cm^{-1} at a resolution of 4 cm^{-1} (16 scans collected). X-ray diffraction (XRD) measurements were carried out on powdered samples with a Bruker D8 diffractometer by using monochromatic $\text{Cu-K}_{\alpha 1}$ radiation ($k = 1.54 \text{ \AA}$) over a 2θ range of 2–80. SEM images were obtained with an FE-SEM (Hitachi S-4300) at an acceleration voltage of 10 kV.

Steady-state luminescence spectra and the lifetime measurements were measured with an Edinburgh Instruments FS920P 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 RMP928 photomultiplier tube.

Supporting Information (see footnote on the first page of this article): Emission spectrum of undoped, bridged, polysilsesquioxane MICPTES-Hb.

Acknowledgments

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