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PAPER

Preparation and luminescence of europium(III) terpyridine complex-bridged polysilsesquioxanes

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Luminescent europium(III) terpyridine complex-bridged polysilsesquioxanes were prepared by hydrolysis and condensation of a precursor composed of a terpyridyl ligand bearing a urea group and a reactive siloxane part in the presence of europium(III) salts. Elementary analysis, FT-IR, SEM, luminescence spectra and luminescence decay analysis were employed to characterize the resulting materials. The effect of counteranions in the europium(III) salts on the morphology and luminescent properties of polysilsesquioxanes is investigated and discussed. It has been shown that porous europium(III) terpyridine complex-bridged polysilsesquioxanes can be obtained with $\text{Eu}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$ whereas materials composed of irregular and aggregated nanoparticles are achieved when the perchlorate counteranions were replaced by chloride ones. The decay time of Eu^{3+} ions of the luminescent materials becomes longer as the molar ratio of the precursor to Eu^{3+} ions increases.

Introduction

Lanthanide complexes are well known efficient molecular luminescent materials, which emit a long-living narrow band of practically monochromatic radiation through the strong optical absorption in the ultraviolet region by the ligands and effective energy transfer from the ligands to Ln^{3+} ions. These properties are favorable in technological application including optoelectronic devices and flat panel displays.^{1–4} Nevertheless, they have not so far been used extensively in practical applications as tunable solid-state lasers or phosphor devices mainly due to their poor thermal stabilities and low-mechanical strength.⁵ Encapsulation of these complexes into sol–gel-derived materials can circumvent these shortcomings and can therefore lead to lanthanide-based luminescent hybrid materials.^{6–14} Two main strategies are employed to realize the hybrid materials so far: (1) simple incorporation of lanthanide complexes into silica gels and (2) covalent grafting of the complex to a silica matrix *via* strong Si–C covalent bonds. Homogeneous distribution of the lanthanide complexes and the prevention of leaching of them from the matrices can be realized by employing the latter method. In general, this is achieved through the co-condensation of TEOS and a hydrolysable alkoxy-silyl derivative that can coordinate to the lanthanide ions. Compared with the hybrid silicates obtained by the co-condensation method, bridged silsesquioxanes are more attractive since the exclusion of TEOS can result in more tethered organic species on the rigid framework.¹⁵

Bridged polysilsesquioxanes are a new class of hybrid organic–inorganic materials obtained through the sol–gel processing of monomers containing a variable organic bridging group and trifunctional silyl groups. The properties of these groups can therefore be tuned by the insertion of appropriate organic functionality into the silicate network through covalent linkage since the organic bridging group can be varied in composition, length, rigidity, and functionality.¹⁶ This can be easily done *via* design and synthesis of desired monomers. As a consequence, bridged silsesquioxanes have found potential applications in optical devices, high-capacity absorbents, catalysts and proton-conducting media for fuel cells.¹⁷

Various dyes have recently been incorporated into the bridging groups of the polysilsesquioxanes with the aim to develop new optical material. The use of dye molecules as bridging groups offers a high loading of chromospheres and avoids leaching or phase separation of the dye molecule.¹⁸ However, much less attention has been paid on the incorporation of luminescent lanthanide complexes in the bridging groups of polysilsesquioxanes.¹⁹ We^{20,21} recently prepared bridged silsesquioxanes exhibiting characteristic emission of lanthanide ions through the hydrolysis and condensation of the monomer containing 2,2-bipyridine or β -diketonate that can coordinate to lanthanide ions and can sensitize the luminescence of them. Results show that the luminescent properties and morphology of the obtained materials can be tuned by changing the monomer or/and changing the experimental conditions. To the best of our knowledge, bridged polysilsesquioxanes with lanthanide terpyridine complexes as the bridging moieties have never been explored. Complexes of terpyridine with metal ions are a very interesting topic of research both for their rich chemistry and physics and for their numerous applications in molecular

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electronics, sensing, extraction, supramolecular chemistry and polymers.²² Especially, lanthanide ions complexed with terpyridine possess additional luminescent characteristics, which can be useful in labeling complex structures of biological importance.²³

In this contribution, we report a novel bridged polysilsesquioxane with luminescent terpyridine lanthanide complexes as the organic bridging group prepared by hydrolysis and condensation of a precursor containing terpyridine moieties in the presence of europium(III) salts as outlined in Scheme 1.

Experimental

Materials

4'-Chloro-2,2':6',2''-terpyridine (J&K Chemica) and 5-amino-1-pentanol (Aldrich) were used as received. $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{Eu}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$ were obtained by dissolving Eu_2O_3 in HCl solution (37%) and dilute HClO_4 solution (1 mol L^{-1}).

Synthesis of compound 1

1 was synthesized according to the modified procedure reported previously and described as follows:²⁴ to a stirred suspension of powdered KOH (2.00 g, 35.6 mmol) in dry DMSO (30 mL) at 60 °C, 5-amino-1-pentanol (770 mg, 7.47 mmol) was added. After 30 min, 4'-chloro-2,2':6',2''-terpyridine was added (2.00 g, 7.47 mmol) and the mixture was stirred for 36 h to produce a dark brown solution. After cooling to 25 °C, the mixture was poured into 600 mL of distilled water to precipitate a pale yellow solid that was filtered, washed with water and then dried in vacuum overnight.

Synthesis of precursor (Terpy-Si)

To a stirred yellow solution, 0.58 g (1.73 mmol) of **1** dissolved in 30 mL of CHCl_3 , 0.51 g (2.08 mmol) of 3-(triethoxysilyl)propyl isocyanate was added and the mixture was refluxed for 12 h under nitrogen atmosphere. The solvent was evaporated and then the precipitate washed with *n*-hexane three times. The white precipitate was centrifuged and then dried *in vacuo* to give **Terpy-Si**. Mp 91.5 °C; ^1H NMR (CDCl_3) δ 8.69 (d, 2H, ArH), 8.62 (d,

2H, ArH), 8.00 (s, 2H, ArH), 7.86 (t, 2H, ArH), 7.34 (m, 2H, ArH), 4.47 (s, 1H, NH), 4.33 (s, 1H, NH), 4.22 (t, 2H, $-\text{CH}_2-$), 3.81 (q, 6H, $-\text{CH}_2-\text{CH}_3-$), 3.20 (m, 4H, $-\text{CH}_2-\text{CH}_2-$), 1.87 (m, 2H, $-\text{CH}_2-\text{CH}_2-$), 1.60 (m, 6H, $-\text{CH}_2-\text{CH}_2-$), 1.22 (t, 9H, $-\text{CH}_3$), 0.63 (m, 2H, $-\text{CH}_2-\text{CH}_2-\text{Si}-$).

Preparation of luminescent materials

Terpy-Si-Eu(ClO₄)₃-1 and **Terpy-Si-Eu(ClO₄)₃-2**. To a solution of **Terpy-Si** (0.45 mmol) in THF (3 mL), an appropriate amount of $\text{Eu}(\text{ClO}_4)_3$ in EtOH was added drop-wise over a period of 3 min under stirring and a precipitate appeared immediately. After the addition is complete, the yellowish precipitate was aggregated into a gel-like solid. 3 mL of H_2O (pH = 1) was then added and the mixture was heated for 24 h under nitrogen atmosphere, some of the solids disappeared during the heating process. The precipitate was recovered by filtration and washed with EtOH three times, dried overnight at 80 °C. The molar ratio of **Terpy-Si** to $\text{Eu}(\text{ClO}_4)_3$ was set as 1 : 1 and 2 : 1, the resulting luminescent material was denoted as **Terpy-Si-Eu(ClO₄)₃-1** and **Terpy-Si-Eu(ClO₄)₃-2**, respectively.

Terpy-Si-EuCl₃-1 and **Terpy-Si-EuCl₃-2**. **Terpy-Si-EuCl₃-1** and **Terpy-Si-EuCl₃-2** were prepared similarly except that $\text{Eu}(\text{ClO}_4)_3$ was replaced with EuCl_3 . The molar ratio of **Terpy-Si** to EuCl_3 was set as 1 : 1 and 2 : 1, the resulting luminescent material was denoted as **Terpy-Si-EuCl₃-1** and **Terpy-Si-EuCl₃-2**, respectively.

The molar ratios of Eu^{3+} ions to terpyridine ligand in the four samples were determined to be 0.85, 0.40, 0.90 and 0.45 for **Terpy-Si-Eu(ClO₄)₃-1**, **Terpy-Si-Eu(ClO₄)₃-2**, **Terpy-Si-EuCl₃-1** and **Terpy-Si-EuCl₃-2**, respectively.

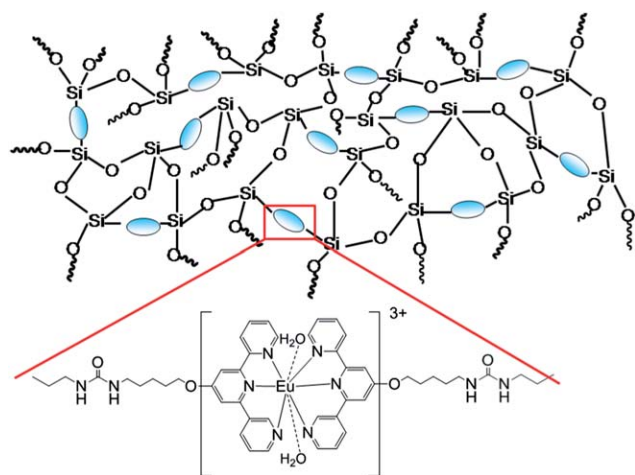
Characterization

Infrared (FTIR) spectra were obtained on a Bruker Vector 22 spectrometer using KBr pellets for solid samples; from 400–4000 cm^{-1} at a resolution of 4 cm^{-1} (16 scans collected), about 2 mg of each compound was mixed with potassium bromide (Merck, spectroscopic grade) finely ground and pressed into pellets. Elemental analysis was performed on a Elementar Vario EI and the contents of Eu^{3+} ions were determined by ICP-AES. SEM images were obtained from an FE-SEM (Hitachi S-4300) at an acceleration voltage of 10 kV. The samples were ground to powder before SEM measurement. The steady-state luminescence spectra and the lifetime measurements were measured on 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 Hamamatsu RMP928 photomultiplier tube.

Results and discussion

FT-IR spectra

The FT-IR spectrum of the precursor **Terpy-Si** (Fig. 1a) shows vibrations characteristic of H-bonded urea groups: $\nu_{\text{N-H}} = 3337$, $\nu_{\text{C=O}}$ (amide I) = 1624 and $\delta_{\text{N-H}}$ (amide II) = 1583 cm^{-1} . Bands at 1598 and 1562 cm^{-1} correspond to the C=C and C=N bonds



Scheme 1 Predicted structure of the europium(III) terpyridine complex-bridged polysilsesquioxanes.

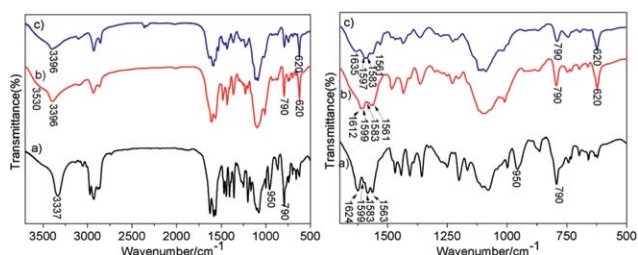


Fig. 1 FT-IR spectra of the precursor **Terpy-Si** (a), the luminescent material **Terpy-Si-Eu(ClO₄)₃-1** (b) and **Terpy-Si-Eu(ClO₄)₃-2** (c).

stretching in the pyridine ring and a strong peak at 790 cm^{-1} indicates the presence of a C–C bond between rings.²⁵ Bands at 1166 and 956 cm^{-1} can be ascribed to the absorption of $\text{SiOCH}_2\text{CH}_3$ groups. The hydrolysis and condensation of the precursor can be confirmed by the disappearance of bands at 956 and 1166 cm^{-1} and the appearance of the broad band at 1020 cm^{-1} assigned to the Si–O–Si (Fig. 1b).²⁶ The vibration of C=O experiences a downshift of 1624 cm^{-1} to 1612 cm^{-1} upon the introduction of $\text{Eu}(\text{ClO}_4)_3$ (molar ratio of precursor to $\text{Eu}(\text{ClO}_4)_3 = 1$), implying that at least part of Eu^{3+} ions are coordinated to C=O groups. The shift of bands in the region of $1300\text{--}1500\text{ cm}^{-1}$ can also be observed if we compare Fig. 1b with Fig. 1a, which indicates that Eu^{3+} ions are also coordinated to the terpyridine groups bonded to silica frameworks. Further increase in the molar ratio of precursor to $\text{Eu}(\text{ClO}_4)_3$ from 1 to 2 leads to an upshift of $\nu_{\text{C=O}}$ vibration to 1635 cm^{-1} , which means that the coordination of Eu^{3+} with terpyridine might influence the strength of H-bonding of the urea groups. Furthermore, bands at 620 cm^{-1} due to the absorption of ClO_4^- can be observed in Fig. 1b and c. Similar trend in the FT-IR spectra (Fig. 2) can also be observed when the perchlorate counteranions were replaced by chloride ones.

Morphology

Fig. 3 shows SEM images of samples derived from hydrolysis and condensation of the precursor in the presence of $\text{Eu}(\text{ClO}_4)_3$. Very interestingly, macroscopic void spaces with polydispersed size can be observed from the SEM images of the obtained samples. Smaller voids can be found inside the larger one if we took a closer look at the SEM images of the sample (the inset in Fig. 2b). Increasing the molar ratio of precursor to Eu^{3+} ions from 1 to 2 results in materials with similar morphology and textures as shown in Fig. 3(a, b) and (c, d). Similar macroscopic

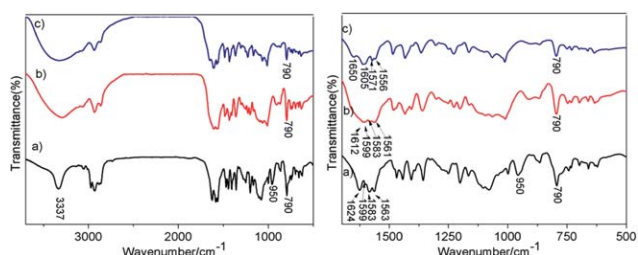


Fig. 2 FT-IR spectra of the precursor **Terpy-Si** (a), the luminescent material **Terpy-Si-EuCl₃-1** (b) and **Terpy-Si-EuCl₃-2** (c).

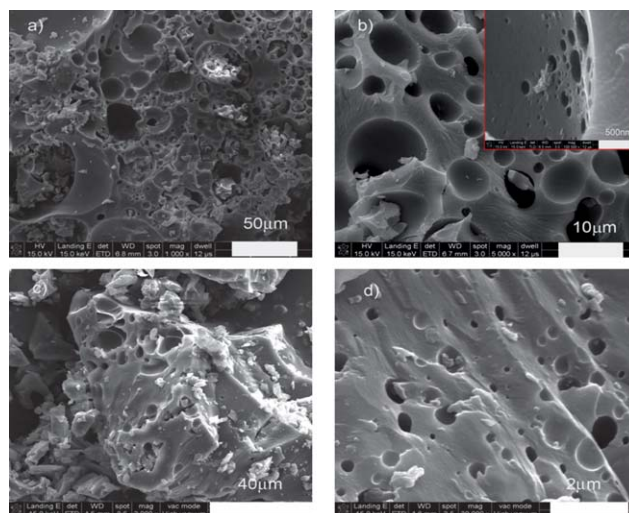


Fig. 3 SEM images of the luminescent material **Terpy-Si-Eu(ClO₄)₃-1** (a and b) and **Terpy-Si-Eu(ClO₄)₃-2** (c and d).

void spaces have been observed previously in the sol–gel-derived organosilica, which was realized through a concentrated direct emulsion, *i.e.*, dispersion of oil (decane) in water.²⁷ Therefore, it is reasonable to assume that the macroscopic void spaces were formed *via* similar mechanisms, the short polymers due to the hydrolysis of monomer (or possibly the complexes of precursor and Eu^{3+} ions) can act as the oil phase. Porous organosilica prepared *via* the oil-in-water emulsion where the short polymer resulting from the hydrolysis of 3-mercaptopropyl trimethoxysilane has been reported.²⁸ However, the counteranions of europium(III) salt can exert significant influence on the morphology of the resulting materials. Replacing perchlorate counteranions with chloride while keeping other conditions unchanged leads to materials with totally different morphology and textures as shown in Fig. 4 which reveals that the materials are composed of irregular and aggregated nanoparticles, whereas changing the molar ratio of precursor to Eu^{3+} ions has no obvious influence on the texture of the materials.

Optical properties

Fig. 5 shows the excitation and emission spectra of the obtained materials. Room-temperature excitation spectra of the samples monitored around the most intense emission line of Eu^{3+} exhibit broad bands in the region of 200 to 390 nm peaking at 250 and

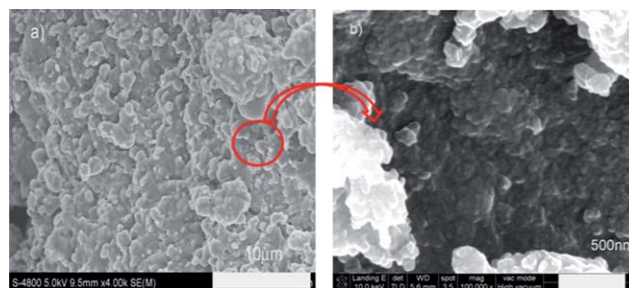


Fig. 4 SEM images of the luminescent material **Terpy-Si-EuCl₃-1** (a) and **Terpy-Si-EuCl₃-2** (b).

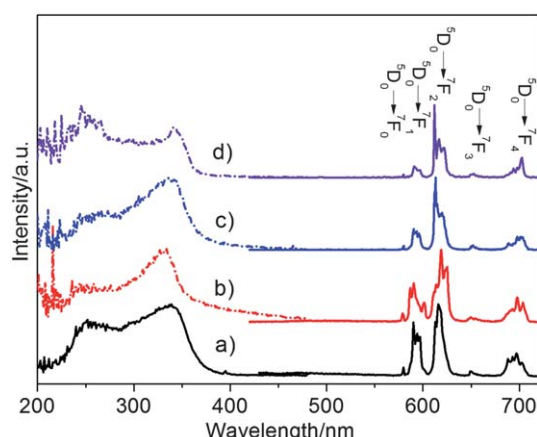


Fig. 5 Excitation (···) and emission (—) spectra of luminescent materials **Terpy-Si-Eu(ClO₄)₃-1** (a), **Terpy-Si-Eu(ClO₄)₃-2** (b), **Terpy-Si-EuCl₃-1** (c) and **Terpy-Si-EuCl₃-2** (d). The excitation spectra were obtained by monitoring ~615 nm and the emission spectra were excited at 340 nm. All spectra were measured at room temperature.

340 nm respectively, which may result from the absorption of terpyridine moieties. Furthermore, self-absorption of Eu^{3+} at 395 nm assigned to ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$ can also be observed, the lower relative intensity of the Eu^{3+} ion compared with that of the terpyridine moieties strongly suggests that the metal ions are essentially excited by a sensitized process rather than by direct population of the intra- $4f^6$ levels. Excitation into the absorption of terpyridine moieties at 340 nm leads to an emission spectrum composed of the characteristic sharp peaks of the Eu^{3+} ${}^5\text{D}_0 \rightarrow {}^7\text{F}_{0-4}$ transitions with the hypersensitive ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition as the most prominent line, which suggests that Eu^{3+} sites are indeed without a center of inversion. In addition, the crystal-field structure of the emission spectra reveals that the site symmetry of Eu^{3+} ions is low, possibly C_{2v} or even lower.²⁹ The ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ line is a parity-allowed magnetic dipole transition and is to a large extent independent of the local symmetry of the Eu^{3+} ions, it therefore can be used for the normalization.³⁰ The intensity ratios (R) of the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ and ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ transitions can be taken as a measure of the asymmetry of the Eu^{3+} sites and it tends to be zero when the excited ions are located at a symmetry site. It is believed that the value of R becomes larger as the interaction of Eu^{3+} with its neighbors becomes stronger and the Eu^{3+} site symmetry becomes lower.³¹ From the emission spectra, we found that the value of R increases from 1.60 to 2.05 as the molar ratio of $\text{Eu}(\text{ClO}_4)_3$ to the precursor increases from 1 to 2 (Table 1).

Table 1 Intensity ratios (R) of $I({}^5\text{D}_0 \rightarrow {}^7\text{F}_2)/I({}^5\text{D}_0 \rightarrow {}^7\text{F}_1)$ and lifetimes of Eu^{3+} in the samples

Sample	R	τ_1	τ_2	τ
Terpy-Si-Eu(ClO₄)₃-1^a	1.60	1.14(74.92%)	0.41(25.07%)	0.78 ^b
Terpy-Si-Eu(ClO₄)₃-2	2.05	—	—	1.25
Terpy-Si-EuCl₃-1^a	3.30	1.24(50.33%)	0.41(49.66%)	0.99 ^b
Terpy-Si-EuCl₃-2	5.48	—	—	1.05

^a The decay curve can be fitted well by $I = I_0 + A_1 \exp(-(t - t_0)/\tau_1) + A_2 \exp(-(t - t_0)/\tau_2)$. ^b Average data obtained according to the equation: $t = (A_1 \tau_1^2 + A_2 \tau_2^2)/(A_1 \tau_1 + A_2 \tau_2)$.

Furthermore, replacing the perchlorate counteranions with the chloride ones leads to a great increase in the R value from 1.60 to 3.30 for samples where the molar ratio of the precursor to Eu^{3+} ions is 1 and from 2.05 to 5.48 for the sample with the molar ratio being 2. The data reveal that a lower symmetry and a larger europium–ligand interaction can be obtained when the terpyridine moieties in the samples increase and/or the perchlorate counteranions are replaced with the chloride ones.

In order to further investigate the luminescence performance of the samples, the lifetime of Eu^{3+} ions in the samples is also measured. The decay curve of Eu^{3+} ions for **Terpy-Si-Eu(ClO₄)₃-1** and **Terpy-Si-EuCl₃-1** can be well fitted to a bi-exponential function, implying the existence of two kinds of Eu^{3+} sites in the materials. The population corresponding to short/long lifetime for **Terpy-Si-Eu(ClO₄)₃-1** and **Terpy-Si-EuCl₃-1** is around 1/3 and 1 respectively, whereas that of **Terpy-Si-Eu(ClO₄)₃-2** and **Terpy-Si-EuCl₃-2** is found to be mono-exponential, revealing only one type of site for the Eu^{3+} in both samples. The lifetime of excited state of Eu^{3+} for all the samples is listed in Table 1, which reveals that the lifetime increases with increasing the molar ratio of the precursor (*i.e.*, terpyridine) to Eu^{3+} ions. This might be due to the coordination of Eu^{3+} ions and the displacement of the coordinating water molecules in the first coordination sphere since water molecules provide an efficient route for the radiationless deactivation.³² Some values of the lifetime reported here are much longer than that of Eu^{3+} ions in polysilsesquioxanes reported by us and others, implying that the Eu^{3+} ions are much better protected from the environment such as water molecules or OH groups as illustrated in Scheme 1.

Conclusions

In summary, we have obtained novel europium(III) terpyridine complex-bridged polysilsesquioxanes through the sol–gel processing of monomers consisted of a terpyridine ligand that has the ability to coordinate and sensitize Eu^{3+} ions and a reactive siloxane that can undergo hydrolysis and condensation to form organosilica gels. The novel luminescent materials are suited to cooperate with UV emitting LEDs because they can be excited in the near UV region. The morphology and luminescent behavior of the obtained materials can be tuned by changing the counteranions of the europium(III) salts. It has been reported previously that crystalline bridged polysilsesquioxanes can be realized through the combination of hydrogen-bonding from the urea group of the precursor and hydrophobic interaction when the carbon chain length of the precursor is long enough.³³ We are currently synthesizing precursors similar to **Terpy-Si** but with a much longer carbon chain to test if a crystalline lanthanide complex-bridged polysilsesquioxane displaying strong emission can be obtained.

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