



# Construction and photoluminescence of amorphous silicone resins containing lanthanide ions as luminescent center

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## ABSTRACT

Three series of luminescent silicone resins have been synthesized. This ternary resin (SiPy-La-L, La = Eu, Tb or Dy; L = 1, 10-phenanthroline or acetylacetonate) is composed from the precursor, the second ligand and lanthanide ions using a sol-gel method. The precursor is derived from the hydrosilylation reaction of methyl-dichlorosilane and 4-vinylpyridine. Lanthanide ions ( $\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$  and  $\text{Dy}^{3+}$ ) act as luminescent center. Structure and texture of silicone resins are characterized by the X-ray diffraction (XRD) and scanning electron microscopy (SEM). The luminescence of silicone resins are monitored and studied in detail. Red and green luminescences are checked when silicone resins are exposed to ultraviolet light, suggesting that the intramolecular energy-transfer processes take place within these silicone resins.

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## 1. Introduction

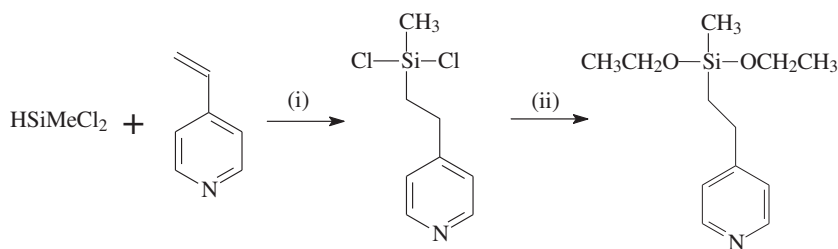
Luminescent materials have many useful applications, including light-emitting diodes (LEDs), biological imaging, sensory devices, displays, tunable lasers and amplifiers for communication [1–6]. It is difficult to obtain pure emission colors from organic chromophore, such as small organic molecules or conjugated polymers. Because their emission spectra typically have a full width at half maximum (FWHM) of 50–200 nm [7]. Nevertheless, lanthanide ions and their complexes have narrow width emission spectra (FWHM < 20 nm). Complex of lanthanide ions with certain organic ligand has two beneficial effects, which are protecting metal ions from vibration coupling and increasing light absorption cross section by “antenna effects” [8]. In such cases, the organic ligand absorbs exciting radiation, undergoes intersystem crossing into a triple state, and then transfers its energy to the lanthanide emitter. The systems like beta-diketone, 1,10-phenanthroline (Phen) and 2,2'-bipyridine (bpy) are well known as light-harvesting ligands for lanthanide ions and can provide extensive photophysical applications. They are optimized antenna of near-UV radiation due to efficient ligand-to-metal intramolecular energy transfer to lanthanide ions ( $\text{Tb}^{3+}$  and  $\text{Eu}^{3+}$ ) [9,10].

Organic ligand-lanthanide ion complexes can be protected from moisture and mild high temperatures at a certain extent when incorporated into inorganic matrices, such as sol-gel silica [2]. The common solution is to link lanthanide complexes and inorganic parts together with covalent or non-covalent bonds [11–20]. Because of their excellent stabilities and mechanical behaviors, silicone- and siloxane-based materials can serve as versatile hosts [11,12]. As a

limited number of silane coupling agents were available, modifications of pre-prepared siloxane precursors with the appropriate organic groups to form new functional resin materials are reported mainly on five paths. There are amino-modification [13–15], carboxylic-modification [16,17], sulfonic-modification [18], sulfide-modification [19] and hydroxyl-modification [20]. Therefore, the research on the design and synthesis of new siloxane precursors will expand the multiplicity of the functional resin materials. Recently we have proposed a simple way that can attach desired organic chelating groups to siloxane precursors via a hydrosilylation reaction of methyl-dichlorosilane [21]. This method is particularly adapted to the preparation of organic/inorganic resin composites because of the possibility of tailoring compounds by mixing organic and inorganic components into a single material at room temperature and in the nanometer scale.

In this paper, we describe the preparation of ternary luminescent functionalized silicone resin material based on lanthanide ion complexes of pyridine group and the second ligands. The precursor was derived from the hydrosilylation reaction between methyl-dichlorosilane and 4-vinylpyridine [21–23]. Then the precursor was submitted to complex with lanthanide ions and second ligands. We chose 1,10-phenanthroline (Phen for short) and acetylacetonate (Acac for short) as the second ligand because they could sensitize the emissions of lanthanide ions. Synthesis, purification, characterization and utilities of the ternary complex of lanthanide ions have been reported elsewhere in detail [12,13,24–26]. And the theoretical calculation about the energy levels and energy transition in these complexes are also researched [27]. The sensitization process took place in these systems. It is described as follows: the ligand absorbs energy, undergoes intersystem crossing into a triple state, and transfers its energy to the lanthanide ions with high efficiency. Then the emission from the lanthanide ions' excited state will be observed. Generally,

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**Scheme 1.** The preparation of pyridine-functionalized siloxane precursor. (i)  $\text{CuCl}_2$ ,  $\text{N,N,N',N'}$ -tetramethylethylenediamine, reflux, 16 h (ii) ethyl orthoformate, reflux.

**Table 1**  
The ratio of reactants in four series of resin materials.

Resins	Lanthanide	Siloxane	Second ligand/mmol		Tetraethoxy silane/mmol
	Nitrate/mmol	Precursor/mmol	Phen	Acac	
I	0.2	0.2	0.6	–	0.4
II	0.2	0.2	0.2	–	0.4
III	0.2	0.2	–	0.6	0.4
IV	0.2	0.2	–	0.2	0.4

this mechanism was also called as antenna effect [8]. After sol-gel process, the antipant silicone resins were obtained. They are generally performed at room temperature where gel particles are stabilized by chemical cross-linking. The structures of the deposited silica particles depend on the ratio of reactants. This work is a continuation of our previous studies on luminescent functionalized silicone resin [17–21]. We wish to generate a general procedure that can be used to synthesize luminescent materials with different quantity of various functional groups.

## 2. Experimental procedure

### 2.1. Sample preparation

Pyridine-functionalized siloxane precursor (SiPy) was synthesized by hydrosilylation reaction between methylchlorosilane and 4-vinylpyridine which process had been published in our paper (see Scheme 1) [21]. Then stoichiometric amount of pyridine-functionalized siloxane precursor, lanthanide nitrates and the second ligands were added to 5 mL ethanol simultaneously. The amounts of the reactants are listed in Table 1. The mixture was agitated magnetically to achieve a single phase in a covered vessel for 4 h, and then 5 mL water was added under gentle magnetic stirring (1 h) to form a multi-interphase emulsion. After that, it was dried on a vacuum line at 60 °C immediately. After aged until the onset of gel, the gels were collected for the physical properties studies. All the samples of these resins are opaque solid powders. The materials came from pyridine-functionalized siloxane precursor, europium ions and 1, 10-phenanthroline were named SiPy-Eu-Phen (the ratio of  $\text{Eu}^{3+}$  ions to Phen is 1:1) or SiPy-Eu-Phen<sub>3</sub> (the ratio

of  $\text{Eu}^{3+}$  ions to Phen is 1:3). And other silicone resins were named in the same manner (see Scheme 2).

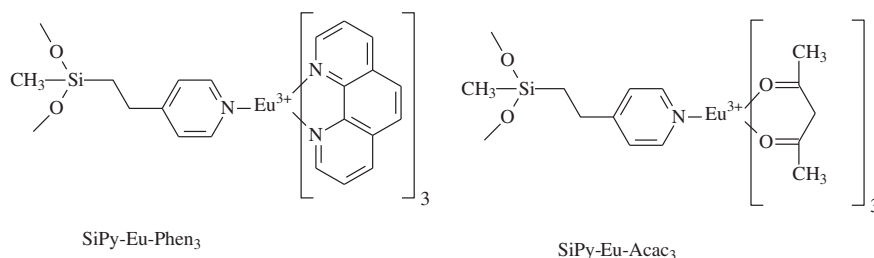
### 2.2. Measurements

Luminescence (excitation and emission) spectra of solid complexes were determined with a Perkin-Elmer LS-55 spectrophotometer whose excitation and emission slits were 10 and 5 nm, respectively. The X-ray diffraction (XRD) measurements were carried out on powdered samples via a “BRUKER D8” diffractometer (40 mA–40 kV) using monochromated  $\text{Cu K}\alpha_1$  radiation ( $\lambda = 1.54 \text{ \AA}$ ) over the  $2\theta$  range of  $1^\circ$  to  $10^\circ$  and range of  $10^\circ$  to  $70^\circ$ , respectively. Scanning electronic microscope (SEM) images were obtained with JEOL JSM-7600F.

## 3. Results

Fig. 1 is the excitation spectra and emission spectra of 1, 10-phenanthroline. An excitation band could be found at 346 nm which was attributed to the aromatic group. And a broad emission band occurs at 380 nm which means that 1, 10-phenanthroline could absorb UV light at 346 nm and emission the UV light at 380 nm. Fig. 2 shows the excitation spectra of europium nitrates (a) and SiPy-Eu-Phen<sub>3</sub> resin (b) which were obtained by monitoring the emission of  $\text{Eu}^{3+}$  ions at 617 nm. The dot line in Fig. 2 are the excitation (340 nm, line I) and emission (380 nm, line II) bands of 1, 10-phenanthroline. Because of no organic ligand in its coordination, the europium nitrates show poor excitation abilities around 340 nm and can only be excited around 390 nm. However, the excitation spectrum of SiPy-Eu-Phen<sub>3</sub> resin (b) shows many differences with the spectrum of europium nitrates (a). Absorption band around 340 nm in curve (b) mainly came from organic groups' absorption in the resins, that is, the pyridine group in siloxane precursor and the second ligands. And they display effects on the improvement of the photophysical properties of materials in the following graphs because of the coordination of the europium ions and the ligands.

The emission spectra of europium nitrates (a), SiPy-Eu-Phen<sub>3</sub> resin (b) and SiPy-Eu-Phen resin (c) are shown in Fig. 3. Narrow-width red luminescences were observed in the spectra of them. The emission bands of the materials were related to the transitions among the different levels of  $\text{Eu}^{3+}$ . The levels of europium ion were assigned



**Scheme 2.** Molecular structures of the Europium resins.

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