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# Construction and Photoluminescence of Monophase Hybrid Materials Derived from a Urea-Based Bis-Silylated Bipyridine

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A urea-based bis-silylated bipyridine ligand derived from 4,4′-diamino-2,2′-bipyridine has been prepared. Organic–inorganic hybrid materials with a high loading of lanthanide 2,2-bipyridine moieties were obtained by using the silylated bipyridine as the only siloxane network precursor in the presence of lanthanide ions (or lanthanide complexes). The in-situ formation of lanthanide complexes from lanthanide ions and the silylated bipyridine during the sol–gel processing was confirmed by the luminescence behavior of the obtained hybrid materials and that of the corresponding pure lanthanide complex [$Ln(bpy)_2Cl_3{\cdot}2H_2O$]. Tris(2-thenoyltrifluoroacetonato)europium(III) dihydrate complexes were coupled to the hybrid materials via adduct formation with the nitrogen atoms from bis-silylated bipyridine, and the coordinated water molecules were expelled from the first coordination sphere of the lanthanide(III) ion as revealed by the much longer lifetime of the hybrid material compared with that of the pure tris(2-thenoyltrifluoroacetonato)europium(III).

## Introduction

The incorporation of luminescent centers into sol–gel-derived siloxane hybrid materials has attracted much interest for photonic applications as they potentially combine the optical quality of silica, its thermal stability, and its mechanical strength, together with the optical characteristics of the active molecules.[1–2] Indeed, materials with stable and highly luminescent properties could have many applications including fiber amplifiers, solid-state lasers, and biolabeling.[3–5] The sol–gel technique represents an attractive means of synthesizing such materials since it allows processing into thin films, fibers, or monoliths.[6–7]

Lanthanide complexes entrapped in sol–gel-derived host structures have been described recently. Nevertheless, simple incorporation of lanthanide complexes within silica gels can result in an inhomogeneous dispersion of both components and leaching of dopants.[8–14] A successful alternative approach to obtain luminescent hybrids is to covalently bind the complexes to a silica matrix. The as-derived multifunctional class II hybrid organic–inorganic luminescent materials were monophasic even at a high concentration of organic chelates.[2,5,15–25]

With these methods, we have previously reported on red and green light-emitting hybrid materials by grafting of lanthanide 2,2-bipyridine complex within silica gel.[16] The rigid framework of 2,2-bipyridine and its high affinity toward various cations are attractive features for the construction of tunable chromophores.[26] 2,2-Bipyridine can form chelates with lanthanide ions such as $Tb^{3+}$ and $Eu^{3+}$. In such cases, the organic ligand absorbs exciting radiation and transfers the excitation energy to the lanthanide emitters. Actually, 2,2-bipyridine ligands are antennas of near-UV radiation because of their efficient ligand-to-metal intracomplex energy transfer.[27–28] However, the luminescent hybrid materials were obtained by using both tetraethyl orthosilicate (TEOS) and silylated 2,2-bipyridine as the siloxane network precursors, where only a small proportion of chelating ligand (only up to 20 mol-% of the total siloxane network precursors) can be found.[16] Consequently, the concentration of lanthanide complexes grafted within the silica gel is still relatively low although a stoichiometric amount of lanthanide ions (with respect to silylated bipyridine) can be obtained. Therefore, it is very attractive to prepare luminescent hybrid materials by using silylated chelating ligand as the only siloxane network precursor. Furthermore, although this method is very convenient to covalently graft lanthanide complexes to the matrix, europium bipyridine complexes are not highly desired because the water molecules can deactivate the excited state of the europium ion via radiationless deactivation. Grafting β-diketonate com-

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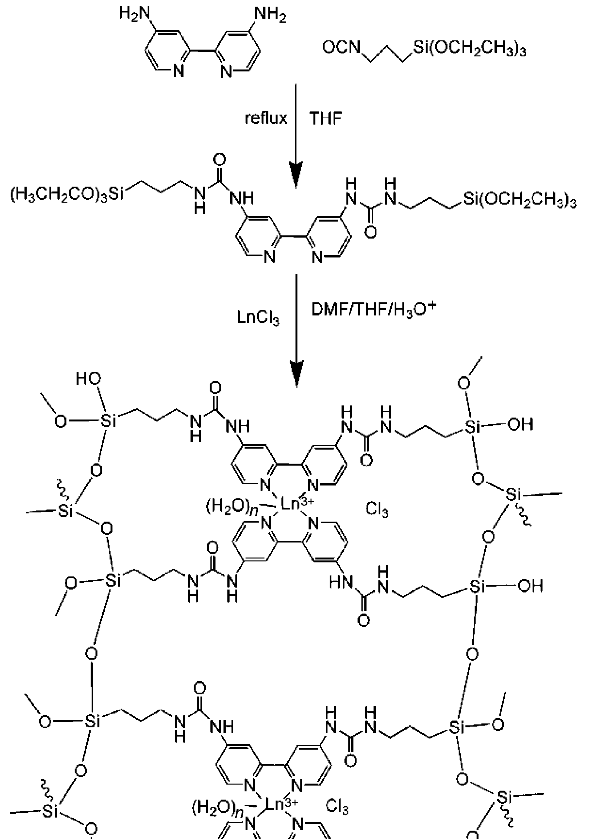
plexes to the silica matrix via adduct formation with the nitrogen atoms from bonded heterocyclic ligands can lead to great improvements in luminescent behavior.[22]

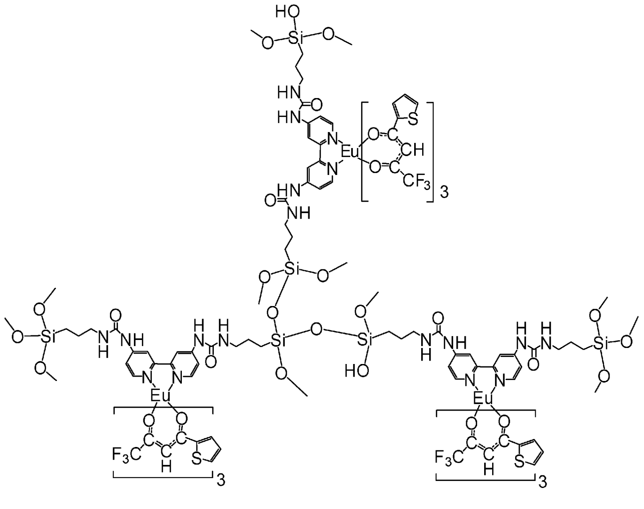
In this paper, the synthesis and characterization of a urea-based bis-silylated bipyridine ligand derived from 4,4′-diamino-2,2′-bipyridine are described. Michel Wong Chi Man has described the synthesis and catalytic properties of the urea-based bis-silylated bipyridine.[29] Luminescent organic–inorganic hybrid materials were obtained by using the silylated bipyridine as the only siloxane network precursor, where lanthanide complexes were formed in situ during the sol–gel processing as revealed by the luminescence behavior of the obtained materials.

## Results and Discussion

The urea-based bis-silylated bipyridine precursor was synthesized from 4,4′-diamino-2,2′-bipyridine and 3-(triethoxysilyl)propyl isocyanate. The bis-silylated bipyridine with the capability of forming one-component hybrid organic–inorganic materials avoided the problem of phase separation. Thus, lanthanide complexes can be anchored to the framework of hybrid organic–inorganic materials by hydrolysis and condensation of the bis-silylated bypyridine in the presence of lanthanide ions or lanthanide complexes (Schemes 1 and 2). All the materials obtained in this work are amorphous as revealed by XRD patterns (not shown) where only a broad peak at about $2\theta = 22$ can be observed.



Scheme 1. Synthesis of the urea-based bis-silylated bipyridine and the predicted structure of Hb-Ln (Ln = Eu,Tb).



Scheme 2. Predicted structure of Hb-Eu-TTA.

Figure 1 shows the FT-IR spectra of Hb and Hb-Eu. In both cases, a ν(Si–C) vibration located in the 1196–1206 cm$^{-1}$ wavelength range is observed, which is consistent with the fact that the (Si–C) bond can survive during hydrolysis/condensation reactions. The broad absorption band at 1120–1000 cm$^{-1}$ [ν(Si–O–Si)] indicates the formation of siloxane bonds and residual silanol groups are evidenced by the ν(Si–OH) stretching vibration at 904 cm$^{-1}$. This means the condensation reactions are not complete as is expected when using organically modified alkoxysilanes as silica network precursors.[2,30] The bands at 1696 and 1535 cm$^{-1}$ can be ascribed to the absorption of –CONH– groups. The bands peaking at 1592 and 1467 cm$^{-1}$ in Figure 1 (a) can be assigned to the absorption of the bpy moieties.[2] Upon the introduction of europium ions, the band from the bpy moieties (1467 cm$^{-1}$) disappears and a new

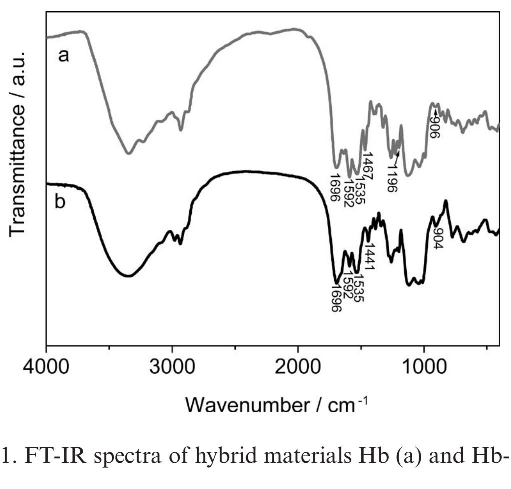


Figure 1. FT-IR spectra of hybrid materials Hb (a) and Hb-Eu (b).

band peaking at 1441 cm$^{-1}$ (Figure 1, b) appears. The new band might be caused by the absorption of bipyridine europium complexes.[31–32]

## Luminescence Properties

The hybrid material Hb-Eu shows a strong red photoluminescence upon irradiation with ultraviolet light. The excitation and emission spectra of Hb-Eu and the lanthanide complex Eu(bpy)$_2$Cl$_3$·2H$_2$O are shown in Figure 2. As anticipated, the hybrid material Hb-Eu shows similar excitation and emission spectral features as the complex Eu(bpy)$_2$Cl$_3$·2H$_2$O. Thus, the proposed schemes are rather speculative and represent illustrative examples of possible coordination (Schemes 1 and 2). The broad band in the excitation spectra can be assigned to the absorption of 2,2-bipyridine. The five prominent emission peaks at 579, 593, 612, 650, and 698 nm in the emission spectra can be attributed to the $^5D_0\rightarrow{}^7F_J$ ($J$ = 0–4) transition with red emission for $J$ = 2 as the dominant feature. There is no evidence for emission from the triplet state of the bipyridine (no broad band emission observed in the blue and green spectral regions). This indicates that there is an efficient energy transfer from the triplet states of the organic ligands to the central europium ion. When the spectra of Hb-Eu and Eu(bpy)$_2$Cl$_3$·2H$_2$O are compared, it is evident that the resolution is better in the case of Eu(bpy)$_2$Cl$_3$·2H$_2$O, and this could be ascribed to the site-to-site inhomogeneities.[22] The lifetimes of the $^5D_0$ Eu$^{3+}$ excited level for Eu(bpy)$_2$Cl$_3$·2H$_2$O and Hb-Eu were measured at room temperature using an excitation wavelength of 325 nm and monitored around the most intense emission line at 613 nm (not shown); the data for both are well fitted by a single exponential function, confirming that all europium ions occupy the same average local environment within each sample. The luminescence lifetimes were determined to be 0.368 ms for the lanthanide complex and 0.459 ms for Hb-Eu. The prolonged lifetime of Hb-Eu compared with that of the lanthanide complex can be ascribed to the fact that the relatively rigid structure of the matrix restricts the vibration of the ligand and thus results in the decrease in nonradiative transition.[33]

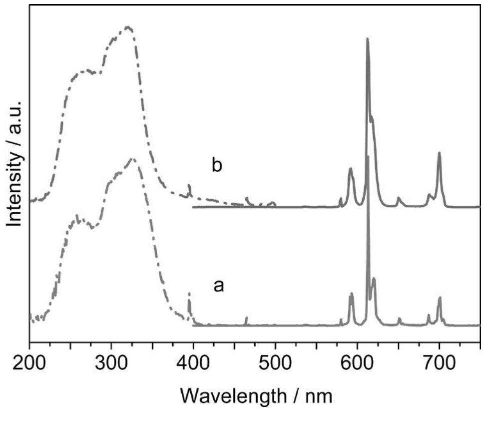


Figure 2. Excitation (dash-dot line) and emission (solid line) spectra of (a) lanthanide complex Eu(bpy)$_2$Cl$_3$·2H$_2$O, and (b) the hybrid material hybrid-Eu.

Replacement of europium ions with the complex Eu(TTA)$_3$·2H$_2$O gives birth to the highly luminescent hybrid material Hb-Eu-TTA. The excitation and emission spectra are shown in Figure 3. The excitation spectrum monitored at 612 nm displays a large broad band and one very low-intensity peak (marked with *) ascribed to an intra-4f$^6$ line. The broad band may result from the $\pi\rightarrow\pi^*$ electron transition of the organic ligand. The lower relative intensity of the Eu$^{3+}$ line strongly suggests that the metal ions are essentially excited via an efficient sensitized process rather than by direct population of the intra-4f$^6$ levels. The luminescence was measured with 325 nm as the excitation wavelength. The emission spectrum is similar to that of hybrid material Hb-Eu. Nevertheless, the intensity ratio of the $^5D_0\rightarrow{}^7F_2$ line to that of the $^5D_0\rightarrow{}^7F_1$ line for Hb-Eu-TTA (15) is much higher than Hb-Eu (4.0). Moreover, 86.5% of the luminescent light output is emitted via the $^5D_0\rightarrow{}^7F_2$ line for Hb-Eu-TTA, while this value is only about 62.9% for Hb-Eu.[34–35] This means that a higher monochromatic purity can be obtained upon the incorporation of Eu(TTA)$_3$·2H$_2$O instead of europium ions. The radiative lifetime of Eu$^{3+}$ in hybrid material Hb-Eu-TTA (0.540 ms) is much longer than in the pure complex Eu(TTA)$_3$·2H$_2$O (0.368 ms) and hybrid material Hb-Eu (0.459 ms). This suggests that the tris(2-thenoyltrifluoroacetonato)europium(III) dihydrate complex was bound to the 2,2-bipyridine groups on the silica gel and the coordinated water was expelled.[22] As a consequence, ternary lanthanide complexes bonded to the silica gel have been formed in situ during the sol–gel processing (Scheme 2).[22] To further confirm the formation of the Eu(tta)3(bpy) complex, the luminescence features of Hb-Eu-TTA were compared with that of Eu(TTA)$_3$(bpy) (see Supporting Information). It is evidenced that excitation and emission spectra of Hb-Eu-TTA are very comparable to those of the pure Eu(TTA)$_3$(bpy) complexes, both the peak positions and the fine structure are the same (Supporting Information). All the experimental data support the hypothesis that Eu(TTA)$_3$(Bpy) complexes are covalently linked to the hybrid organic–inorganic material.

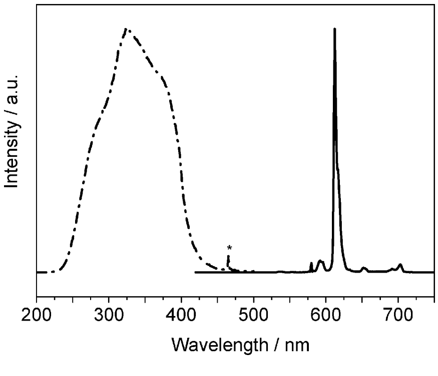


Figure 3. Excitation (dash-dot line) and emission (solid line) spectra of hybrid material Hb-Eu-TTA.

When the europium ions in hybrid material Hb-Eu were replaced by terbium ions, a hybrid material (Hb-Tb) with intense green photoluminescence can be observed. The luminescence behavior of Hb-Tb is similar to that of hybrid material Hb-Eu. As seen in Figure 4, the excitation spectrum monitored at 544 nm is dominated by a broad band with two main components peaking at ca. 254 and 316 nm, respectively, and no f-f transitions can be observed. Excitation into the ligand at 327 nm results in a bright green emission, the line emissions are assigned to the transitions from the $^5D_4$ level to the $^7F_J$ levels ($J = 6, 5, 4, 3$) at 490, 544, 584, and 620 nm, respectively. No emission from the ligand is observed, which indicates that the surrounding ligands absorb energy and transfer energy efficiently to the chelated terbium ions. The decay curve of Hb-Tb was measured under the excitation wavelength that maximizes the emission intensity. The decay curve is well-reproduced by means of a single exponential function, yielding a $^5D_4$-lifetime value of 1.12 ms, which is much longer than that of the pure lanthanide complex [$Tb(bpy)_2Cl_3{\cdot}2H_2O$, $\tau = 0.736$ ms].

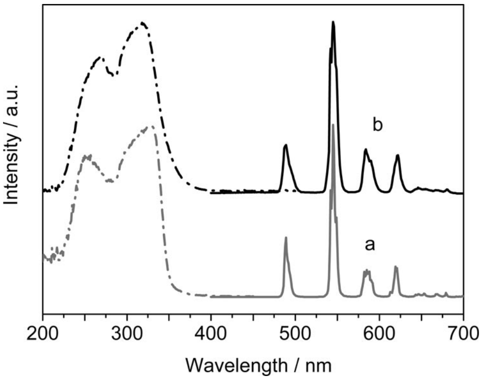


Figure 4. Excitation (dash-dot line) and emission (solid line) spectra of (a) lanthanide complex $Tb(bpy)_2Cl_3{\cdot}2H_2O$, and (b) the hybrid material hybrid-Tb.

In order to further confirm the formation of lanthanide complexes between $Tb^{3+}$ ions with 2,2-bipyridine within the hybrid material, we compared the luminescence properties of Hb-Tb with those of the corresponding pure lanthanide complex [$Tb(bpy)_2Cl_3{\cdot}2H_2O$]. The Hb-Tb material shows a similar excitation spectral feature as the complex $Tb(bpy)_2{\cdot}2H_2O$ and no obvious shift in wavelength of emission line peaks exists. The similarity in luminescence properties further indicates the formation of lanthanide complexes within the sol–gel-derived matrix.

## Conclusions

In summary, new luminescent materials covalently bonded with lanthanide complexes were prepared via an in-situ method by hydrolysis and polycondensation of a urea-based bis-silylated bipyridine precursor in the presence of lanthanide ions or lanthanide complexes. The high concentration of lanthanide complexes grafted to the hybrid silica was anticipated because the silylated bipyridine was used as the only siloxane network precursor. Tris(2-thenoyltrifluoroacetonato)lanthanide(III) dihydrate complexes were coupled to the hybrid materials via adduct formation with the nitrogen atoms from bis-silylated bipyridine.

## Experimental Section

**Starting Materials and Experimental Techniques:** Starting materials were purchased from Aldrich or Fluka and were used as received. All solvents were distilled before utilization according to literature procedures.[35] Lanthanide chlorides were obtained from the corresponding oxides in HCl (37.5%). 4,4′-Diamino-2,2′-bipyridine was synthesized according to a previously reported procedure.[36] The [$Eu(tta)_3{\cdot}2H_2O$] and $Ln(bpy)_2Cl_3{\cdot}2H_2O$ (bpy = 2,2′-bipyridine) complexes were prepared according to the published procedure.[37]

**Synthesis of the Precursor DPS-ICPTES:** 4,4′-Diamino-2,2′-bipyridine (1 mmol) was added to dry tetrahydrofuran (THF; 10 mL). To this mixture 3-(triethoxysilyl)propyl isocyanate (2.4 mmol) was slowly added and the resulting solution was refluxed for 10 h. After evaporation and washing with petroleum ether, a yellow oil of DPS-ICPTES was obtained. Yield 10%. IR (KBr): $\tilde{\nu}$ = –CONH– 1692, 1534; aromatic: 1590, 1467; $SiOCH_2CH_3$: 1166, 956; Si–C: 1198–1205 $cm^{-1}$. $^1H$ NMR ([$D_6$]DMSO): $\delta$ = 8.13 (d, 2 H, $H^{3,3'}$), 7.90 (s, 2 H, $H^{6,6'}$), 7.46 (d, 2 H, $H^{4,4'}$), 7.10 (s, 2 H, NH), 6.5 (brs, 2 H, NH), 3.73 (q, 12 H, $OCH_2$), 3.21 ($t_2$, 4 H, NCH), 1.55 (quint, 4 H, $CH_2$), 1.16 [t, 18 H, $CH_3$(OEt)], 0.55 (t, 4 H, $SiCH_2$) ppm.

**Synthesis of Hybrid Material Hb-Ln (Ln = Eu, Tb):** A solution of $LnCl_3$ in DMF (2 mL) and deionized $H_2O$ (0.5 mL) (acidified to 0.2 M HCl) was added to a DPS-ICPTES solution in THF. The mixture was vigorously stirred at room temperature for 12 h and the volume of solvent was evaporated to ca. 30% of its original size. Then the solution was poured into a flat-bottomed plastic box and was dried at 80 °C for 3 d. A transparent orange solid was obtained. The molar ratio of $Ln^{3+}$ ion to DPS-ICPTES was 1:2.

**Synthesis of Hybrid Material Hb-Eu-TTA:** Hb-Eu-TTA was prepared similarly except that $Eu(tta)_3{\cdot}2H_2O$ was added. The molar ratio of $Eu(tta)_3{\cdot}2H_2O$ to DPS-ICPTES was 1:1.

**Characterization:** Infrared spectra were obtained with a Bruker Vector 22 spectrometer using KBr pellets, 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. X-ray diffraction measurements were carried out on powdered samples with a Bruker D8 diffractometer using monochromatic Cu-$K_\alpha$ radiation ($\lambda$ = 1.540 Å).

The steady-state luminescence spectra and the lifetime measurements were measured with an Edinburgh Instruments FS920P near-infrared 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 also the footnote on the first page of this article): Excitation and emission spectra of Eu(TTA)3(bpy) and hybrid material Hb-Eu-TTA.

## Acknowledgments

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