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Synthesis and optical features of an europium organic–inorganic silicate hybrid

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Abstract

An europium organic–inorganic silicate hybrid was synthesized by grafting a coordinative group (dipicolinic acid) to a silicate network precursor (3-aminopropyltriethoxysilane) via a covalent bonding. Sol–gel process and complexation were performed using different experimental conditions. The hybrid materials, in particular the Eu^{3+} coordination mode, were characterized by infrared and luminescence spectroscopies. Morphology of the materials and TG analysis showed that grafted silica enhanced thermal and mechanical resistances of the organic part. © 1998 Elsevier Science S.A.

Keywords: Hybrid; Organic–inorganic; Synthesis; Grafting; Spectroscopy

1. Introduction

In recent years, luminescent lanthanide (especially Eu^{3+} and Tb^{3+}) chelates have been used as labels in biological applications because of their unique properties: high quantum yields of the emission, large Stokes shifts, long decay times and narrow emission bands. The synthesis of functionally optimal, stable and highly luminescent chelates usable as luminophores for lamps or screens has been a challenge for a number of research groups. Nevertheless, due to their weak thermal and mechanical resistances, these compounds can obviously be excluded for such applications. To improve the desired characteristics, an alternative consists in grafting the organic part on an inorganic host via a covalent bonding. The hybrid formed is expected to combine the high luminescence efficiency and the robust nature of the organic and inorganic components, respectively, which allows such compounds to withstand the conditions present in discharge lamps for example. Similar compounds have been already successfully used in the realization of nonlinear optical systems [1].

The present paper is devoted to the synthesis and spectral characteristics of an europium organic–inorganic silicate hybrid. For this purpose, the complexing agent (a dipicolinic acid derivative) has been double covalently attached through amidation to an organically substituted alkoxysilane ($(EtO)_3Si–(CH_2)_3–NH_2$). The silicate matrix has been obtained by a sol–gel process which is well known to be the most adequate route to prepare organic-inorganic hybrids [2]. The compounds are characterized by infrared spectroscopy and thermogravimetric analysis. The derived results evidence the hybrid character of the synthesized compounds and the enhancement of the thermal resistance.

2. Experimental

2.1. Apparatus

^{1}H and ^{13}C NMR spectra were recorded on a Brüker AC 400. Infrared absorption spectra were recorded as KBr pellets on a Nicolet model 5SXC FT–IR spectrometer. Thermogravimetric analyses were carried out on a TA-50WSI system (Shimadzu) in air, with heating rate of 4°C min^{-1} from 25 to 600°C. Luminescence measurements were performed at various temperatures under several excitation sources using the experimental set-up described elsewhere [3].

2.2. Ligand grafting

All reagents were purchased from Aldrich Chemical Co. or Fluka and used as received; the reaction sketch is given in Fig. 1 (step 1).

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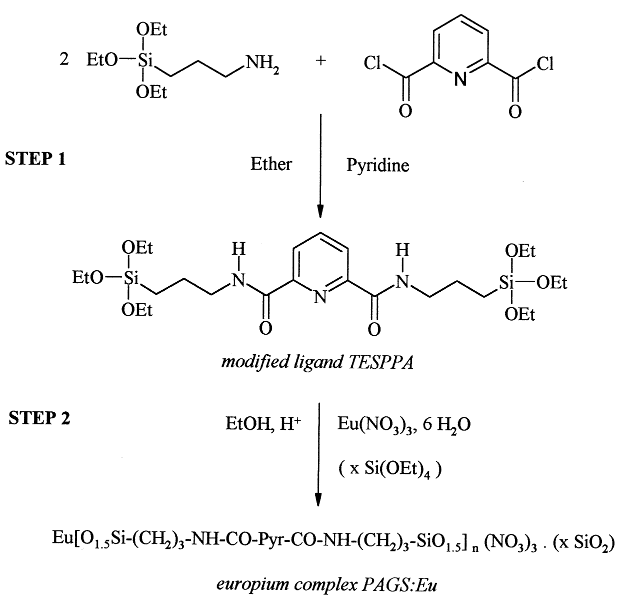

Fig. 1. Synthesis of a europium organic complex-grafted silica.

3-aminopropyltriethoxysilane (4.34 g; 19.6 mmol) was added to a solution of 2,6-pyridinedicarbonyl dichloride (2.0 g; 9.8 mmol) and pyridine (1.70 g; 21.5 mmol) in anhydrous ether (50 ml). The resulting mixture was stirred at room temperature, under argon atmosphere to prevent hydrolysis of the alkoxy groups. After removing the precipitated pyridinium chloride and the solvent, *N,N′*-bis(triethoxysilanepropyl) - 2,6 - pyridine dicarboxamide (modified ligand TESPPA) was isolated (95% yield). The IR, ^{1}H and ^{13}C NMR spectra are in full agreement with the proposed formula. In particular, the amide linkage formation and the presence of the ethoxide groups are clearly demonstrated.

2.3. Sample preparation

For complexation with the modified ligand TESPPA, europium(III) was introduced as a nitrate salt $Eu(NO_3)_3$, $6H_2O$ prepared by reaction of Eu_2O_3 (Rhône-Poulenc; 99.99%) with diluted nitric acid. The hydrated salt provides water which allows the hydrolysis of $Si(OEt)_3$ groups, leading to the inorganic silica network formation by a sol–gel route. Gelation was performed by using HCl as an acid catalyst. Two parameters which may have an effect both on the sol–gel process and on the complexation reaction were investigated here: the concentration of reagents (ratio $n=[\mathrm{TESPPA}]/[Eu(NO_3)_3,\ 6H_2O]$) and the whole content of sol–gel precursor adjusted by the addition of unmodified alkoxide $Si(OEt)_4$ (TEOS) (ratio $x=[\mathrm{TEOS}]/[\mathrm{TESPPA}]$).

Europium hybrid complexes derived from 2,6-pyridine-dicarboxamide-grafted silica (PAGS:Eu) were prepared as described in Fig. 1 (step 2). TESPPA was first dissolved in distilled ethanol, with a small amount of concentrated hydrochloric acid, and the solution was stirred until homogeneous. Appropriate amounts of europium nitrate ethanolic solution was then added so that the ratio *n* ranges from 3 to 10. The resultant solution was stirred for 10 min and was then allowed to stand under cover at room temperature. The immersed gel was filtered off after 3 days, washed several times with distilled water and dried in an oven.

In the case of co-hydrolysis between TESPPA and TEOS, the two different sol–gel precursors were mixed together before dissolution ($x=5$, 10, 20) and the hybrid materials were prepared as above, considering the condition $n=3$. In that case however, the condensation step leads to a monolithic gel which was powdered before use. Gelation times range from 5 days to 2 weeks.

2,6-pyridine dicarboxamide grafted silica without doping (PAGS) was obtained by a simple sol–gel process, using a water amount defined as $[H_2O]/[Si]=3$.

3. Results and discussion

3.1. Characterization of europium hybrid complexes

From the IR measurements, it is possible to characterize both the inorganic silica network and the organic coordinative groups, after submitting the modified ligand to sol–gel process and complexation.

The variations observed in vibration frequencies relative to Si–O bonds are summarized in Table 1 and are presented in Fig. 2. It must be noted that the complexation and sol–gel processes occur without Si–C bond cleavage. The Si–O frequencies displacements prove the silica

Table 1
Assignments of infrared absorptions due to Si–O and Si–C vibrations

	TESPPA (cm^{-1})	PAGS (cm^{-1})	PAGS:Eu, $x=0$ (cm^{-1})	PAGS:Eu, $x\neq 0$ (cm^{-1})
ν(Si–C)	1193	1199	1200	1200
ν(Si–O)	1167	1119	1110	1130
	1103	1083	1080	1072
	1079	1037	1020	
	957			
ν_3		907	908	950
ν_1		789	790	790
ν_4		427	426	450

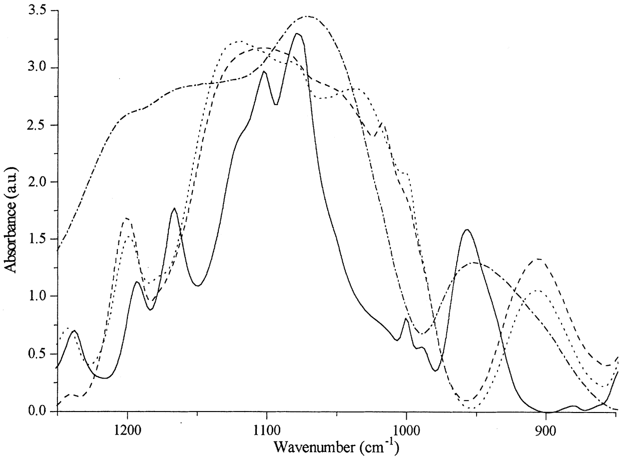

Fig. 2. Evolution of the Si–O stretching vibration frequencies in the 1250–850 cm^{-1} range for: TESPPA (———); PAGS (· · ·); PAGS:Eu with $n=3$ and $x=0$ (– – –), with $n=3$ and $x=10$ (– · –) (see the text for meaning of n and x).

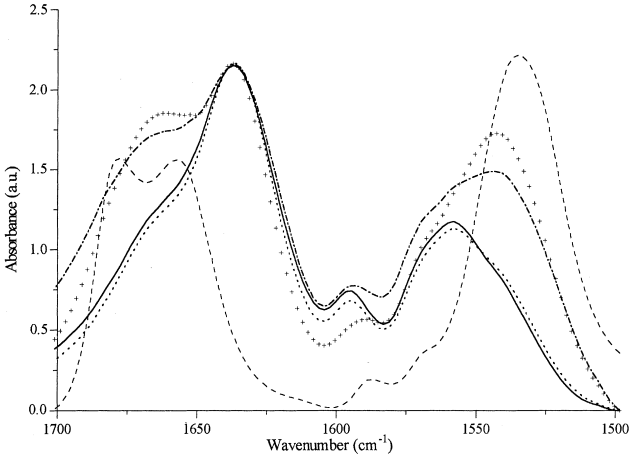

Fig. 3. C=O and C–N absorptions for PAGS:Eu considering different n ratios: $n=3$ (———), $n=4$ (· · ·), $n=6$ (– · –), $n=10$ (+ + +) ($x=0$ in all cases), compared with TESPPA (– – –).

matrix formation whatever reaction condition used. Indeed, the IR spectrum of TESPPA exhibits four absorption bands characteristic of the Si–OEt vibrations (asymmetric stretching) located at 1167, 1102, 1079 and 957 cm^{-1} [4]. IR spectra of PAGS:Eu compounds obtained with different n or x values show a broad absorption in the range 1120–1000 cm^{-1}, which is attributed to the ν(Si–O–Si) asymmetric vibrations. Absorption maximum is observed near 1110 cm^{-1} for $x=0$ and near 1070 cm^{-1} for $x\neq0$. This frequency shift is indicative of more extended siloxane chains, as a consequence of the insertion in the inorganic network of tetrafunctional species in addition to trifunctional ones. ^{29}Si NMR should be useful in determining degrees of condensation in relation with experimental conditions.

The synthesized compounds are always amorphous but their 'texture' may change according to experimental conditions. In particular, it strongly depends on the siloxane chain extent; hydrolysis/condensation reactions give powdered products when $x=0$, whereas monolithic gels were obtained when TEOS is added. Therefore, TEOS can be used as a crosslinking reagent to increase the network rigidity. The different morphologies are connected with gelation durations which increase with decreasing [H_2O]/[Si] ratio, i.e. with increasing n or x ratios.

Infrared absorption frequencies of nitrates and amide groups are given in Table 2. It may be noted that the frequencies observed for the available coordinative groups are very similar for the different x values ($n=3$); only the variations with n ratio are significant and will be discussed in the following section. The decrease of the carbonyl stretching frequency on complexation (1637–1640 cm^{-1} instead of 1660 cm^{-1} for the free ligand) indicates that the grafted ligand coordinates europium (III) ions with the oxygen atoms of the carbonyl groups [5]. Typical infrared spectra in the C=O stretching region are depicted in Fig. 3. For $n=3$, the absorption band relative to ν(C=O) is single; for higher n values, this band is progressively splitted into two components, respectively, assigned to coordinated and free ligand. It suggests that europium(III) environment contains no more than three organic ligands. The increase in the N–C bending frequencies is a further proof of

Table 2
Typical vibration frequencies (in cm^{-1}) of the nitrates and amide groups

	PAGS	PAGS:Eu						
		$n=3/x=0$	$n=4/x=0$	$n=6/x=0$	$n=10/x=0$	$n=3/x=5$	$n=3/x=10$	$n=3/x=20$
ν(NH)	3322	3290	3284	3283	3317	~3300	~3300	~3300
ν(C=O)	1660	1637	1637	1637	1661 1637	1639	1640	1641
	1586	1595	1595	1594	1590	1597	1598	1599
δ(C–N)	1543	1558	1558	1544	1542	1561	1562	1564
ν_3 NO_3^-	—	1459	1459	—	—	1459	1461	1460
	—	1436	1435	—	—	1432	1434	—
Ionic NO_3^-	—	1384	1384	1384	1383	1384	1384	1384
ν_1 NO_3^-	—	1018	1018	(1018)	—	—	—	—
Ionic NO_3^-	—	721	721	720	721	721	720	721
ν_4 NO_3^-	—	661	661	(661)	—	660	661	—

coordination via carbonyl groups but it is less sensitive, particularly for the high *n* values. Considering the ligand structure, we can assume that nitrogen atoms of pyridine groups also take part in europium coordinative environment [6]. This cannot be proved by IR measurements, but only by Raman spectroscopy.

Strong absorption at 1384 cm^{-1} is observed for each compound and was assigned to a free nitrate ion; absorptions at 1459 and 1434 cm^{-1} appear for *n* ratios of 3 and 4, indicating the presence of coordinated nitrate species [7]. Comparison between absorption intensity of coordinated NO_3^- and ionic NO_3^- suggests that the latter are the most predominant species in all cases. Besides, the rather low frequency of coordinated nitrate groups indicates weak coordination.

TG analyses show that grafting the organic ligand to a silica network enables a better thermal stability. For PAGS:Eu, an initial loss of water and residual solvents is noticed at temperatures below 150°C. Decomposition of compounds occurs in a single pathway, in the 300–500°C temperature range; the residue only contains the silicate matrix. For comparison, decomposition is complete at 330°C when siloxane groups are replaced by methyl groups. IR spectra confirm that, up to 300°C, no chemical transformation of the hybrid network occurs and that the Si–C bond is conserved.

3.2. Luminescence properties

Emission spectra were recorded at low temperature under the several excitation sources described in Ref. [3]. All the interpreted spectra are similar exhibiting the same spectral features. They consist in several bands related to the radiative de-excitation from the $^5D_0$ excited level of Eu^{3+}. They are dominated by the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition peaking at 616 nm, which gives an intense red luminescence output for the samples. Careful analysis of the $^5D_0 \rightarrow {}^7F_J$ ($J=1$–2) emission bands shows a lifting of the selection rules since three and five peaks were recorded for $J=1$ and 2, respectively. Such observation indicates that the Eu^{3+} ion lies in a site of low symmetry. Fig. 4 shows, as an example, the time-resolved spectra (TRS) recorded at 15 K for PAGS:Eu ($n=3/x=5$). Care was taken to make sure of the absence of the starting europium nitrate. This latter exhibits an emission spectrum, the wavelength repartition of which is different from the spectra of Fig. 4. On the other hand, their respective luminescence occurs over different range times: 1 ms for the europium nitrate and 6 ms for PAGS:Eu. Such observations confirm that the coordination sphere of the europium has been modified during the synthesis. The luminescence decays of all synthesized samples are exponential with a time constant of 1.1 ms at 15 K while the $^5D_0$ lifetime of trivalent europium in nitrate is much shorter (160 μs).

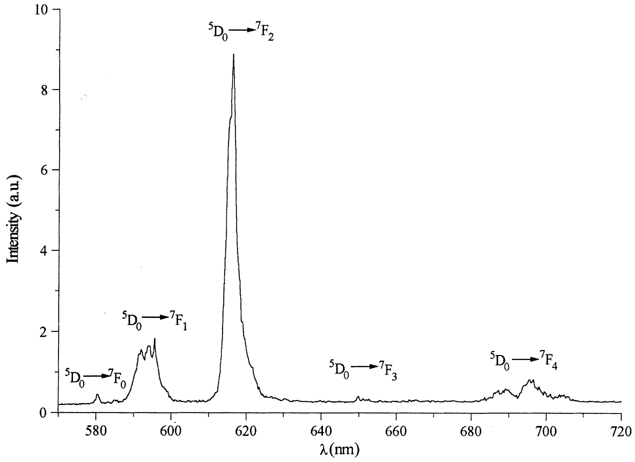

Fig. 4. Eu^{3+} time-resolved fluorescence spectrum of PAGS:Eu ($n=3/x=5$) under excitation at 337.1 nm ($T=15$ K, delay=300 μs, gate=5 μs).

An interesting fact concerns the stability of the compounds. As mentioned in the Section 3.1, PAGS:Eu samples are stable up to 300°C while for the organic part considered alone, the decomposition starts at 150°C approximately. Enhancement of the thermal stability has been considered as a characteristic of the hybrid. On the other hand, destroyed by focusing the laser beam, the simple organic compound becomes brown for energies above 10 μJ, while PAGS:Eu remains unchanged under the same pumping conditions, confirming above-mentioned results.

One may note that the emission intensity and the spectral repartition are the same for the simple organic part and the hybrid materials. Moreover, the emission intensity shows a magnification of about 30 under UV excitation between the europium nitrate and PAGS:Eu, indicating an efficient sensibilization of the emitting center by the organic ligand.

To summarize, an Eu–silicate hybrid has been successfully synthesized using the sol–gel process. Such result is confirmed by IR absorption and supported by luminescence measurements. The enhanced thermal stability comparatively to organic compounds with respect to their luminescence efficiency opens the perspective of realization of new luminescent compounds.

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