

Molecular Design and Fluorescent Whitening Emission from Novel Lanthanide Activated Organic–Inorganic Covalently Hybrid Micro-particles

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Abstract A series of potential lanthanide activated fluorescent-whitening hybrid micro-particles has been prepared by sol-gel method. The precursor derived from 2,2'-dipyridylamine derivative modified through hydrogen transfer addition exhibited a self-organization under the coordination to RE³⁺ (Eu³⁺, Tb³⁺, Sm³⁺, Dy³⁺, respectively) evaluated by SEM (micrometric scale) and X-ray diffraction studies (nanometric scale). The adapting traditional routes used in this paper affected the shape of the materials and can be taken as a new method to control the hydrolysis-polycondensation process. Fourier transform infrared (FTIR), Diffuse reflectance ultraviolet-visible spectra (DRUVS) and ¹H NMR spectra were used to confirm the modifications. These activated phosphors with lanthanide ions represent a novel way to produce fluorescent whitening agents.

Keywords Molecular design · 2,2'-dipyridylamine · Lanthanide organic–inorganic covalently hybrid micro-particles · Fluorescent whitening agent

Introduction

Fluorescent whitening agents (FWAs) is widely used in textile [1], paper [2], polymer materials [3], cosmetics [4]

and plastic manufacturing and in household detergents [5], because of its property to transform part of the UV-visible solar irradiation in a blue fluorescence light, giving the feeling of bright whiteness [6]. Materials treated with the fluorescent whitening agents obtain a high degree of whiteness which cannot be achieved by the common bleaching methods [7]. However, the fluorescent whitening agents migrate with time, and the degree of whiteness decreases. The introduction of unsaturated polymerizable groups into polymer structure has been investigated to overcome this defect. The copolymerization process between unsaturated groups and vinyl monomers resulted in the formation of covalent bonds in the polymer molecule, obtaining structural bleached and fluorescent polymers with resistance to wet treatment and solvents [8–9]. As an alternation, the disposal of linking fluorescent whitening groups and inorganic parts together with covalent bonds is seemed to be feasible. This modification can utilize both parts' properties and the final production can be monophasic even at a high concentration of organic chelates, and the reinforcement of thermal and mechanical resistances has been clearly established [10]. The development of novel linkages for tethering organic compounds to inorganic solid supports has been researched thoroughly and there are four ways to synthesis this kind of hybrid materials: carboxyl-modification [10, 11], amino-modification [12], hydroxyl-modification [13], and sulfonic-modification [14].

Preparing silica-based organic–inorganic hybrid materials by sol-gel method has been taken as a classical approach due to the advantages such as low-temperature processing and easy shaping, higher sample homogeneity and purity [15]. Moreover, the location of the organic dyes can be priori tuned through dye-matrix interactions [16]. Even when all the silica materials obtained by sol-gel route are always amorphous systems, the self-organization process in

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these hybrid materials has been demonstrated by using very specific organic precursors that exhibit a strong interaction by H-bonding [17–19]. The introduction of a linear organic group presenting rigid or semirigid or flexible geometries appeared like a factor favorable for the existence of an organization into these amorphous systems [20–22]. In all the cases investigated, only weak interactions between the organic moieties such as van der Waals, London, or π – π staking were able to induce an organization.

Thus, our specific investigations have concerned about the photochemical behavior of a kind of lanthanide activated fluorescent-whitening hybrid micro-particles. And the structure, as well as the texture, of the hybrid solids would also be investigated to study how the coordination between the ions and the ligands in the sol-gel process can effect on the organization in those amorphous systems. We use 2,2'-dipyridylamine as the organic dyes. It could react with 3-(triethoxysilyl)-propyl isocyanate and then the derived multifunctional organosilane precursor could be afterward submitted to complex with lanthanide ions and to a sol-gel process in order to obtain the anticipant hybrid materials. They are generally performed at room temperature where gelatine nanoparticles have to be stabilized by chemical cross-linking. In this treatment, we developed an oil-in-water emulsion process involving the drying gelatine on a vacuum line, followed by the rapid condensation of silicates, leading to stable hybrid micro-particles.

Experimental section

Chemicals and procedures

Starting materials were purchased from Aldrich or Fluka and were used as received. All normal organic solvents were purchased from China National Medicines Group and were distilled before utilization according to the literature procedures [23]. Terbium, europium, samarium, and dysprosium nitrates were obtained from the corresponding oxides in dilute nitric acid.

The typical procedures for the preparation of hybrid precursor and hybrid material are described in the Scheme 1 (I). The hybrid precursor was prepared as follows: 1.027 g (6 mmol) 2,2'-dipyridylamine was first dissolved in 15 ml pyridine by stirring and then 1.484 g (6 mmol) 3-(triethoxysilyl)-propyl isocyanate was added to the solution by drops. The whole mixture was refluxing at 70 °C for 6 h. The solution was condensed to evaporate the solvent and then the residue was dried on a vacuum line. A yellow oil was obtained. ^1H NMR (CDCl_3 , 500 MHz) 0.64(t, 2H, H_3), 1.22(t, 9H, H_1) 1.64(m, 2H, H_4), 3.18(q, 2H, H_5), 3.84

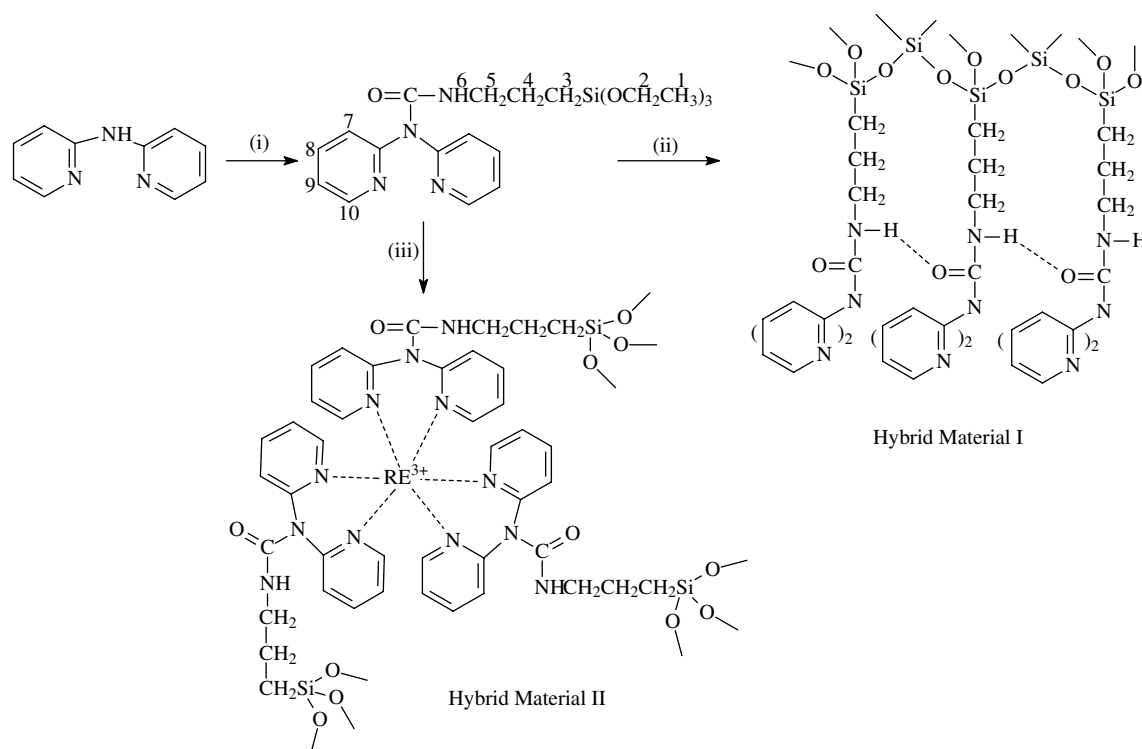
(q, 6H, H_2), 4.98 (t, 1H, H_6), 6.83 (t, 1H, H_9), 7.56 (t, 1H, H_8), 8.26(d, 1H, H_{10}).

The sol-gel derived hybrid was prepared as follows: 0.6 mmol hybrid precursor and 1.2 mmol tetraethoxysilane (TEOS) were dissolved in 5 ml ethanol with stirring. The mixture was agitated magnetically to achieve a single phase in a covered Teflon beaker for four hours, and then 30 ml water was added under gentle magnetic stirring to form an initial o/w (oil-in-water) macro-emulsion for an hour. After that, it was dried on a vacuum line at 60 °C immediately. After aged until the onset of gelation which occurred, the gels were collected for the physical properties studies. It was named hybrid material I in this paper.

The sol-gel derived hybrid containing rare earth ions was prepared as follows: 0.6 mmol hybrid precursor was dissolved in 5 ml ethanol with stirring. Then 0.2 mmol $\text{RE}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ($\text{RE}=\text{Tb}$, Eu , Sm and Dy) and 1.2 mmol tetraethoxysilane (TEOS) was added into the solution respectively. The mixture was agitated magnetically to achieve a single phase in a covered Teflon beaker for four hours, and then 30 ml water was added under gentle magnetic stirring to form an initial o/w (oil-in-water) macro-emulsion for an hour. After that, it was dried on a vacuum line at 60 °C immediately. After aged until the onset of gelation which occurred, the gels were collected for the physical properties studies. And they were named hybrid material II in this paper.

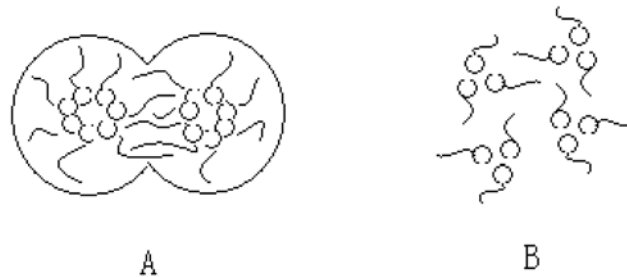
Measurements

Fourier transform infrared (FTIR) spectra were measured within the 4000–400 cm^{-1} region on an (Nicolet model 55XC) infrared spectrophotometer with the KBr pellet technique. ^1H NMR (Proton Nuclear Magnetic Resonance) spectra were recorded in CDCl_3 on a BRUKER AVANCE-500 spectrometer with tetramethylsilane (TMS) as inter reference. Diffuse reflectance ultraviolet-visible spectra (DRUVS) of hybrid materials were recorded with a BWSpec 3.24u_42 spectrophotometer. Phosphorescent spectra (chloroform solution) and luminescence (excitation and emission) spectra of these solid complexes were determined with a RF-5301 spectrophotometer whose excitation and emission slits were 5 and 3 nm, respectively. Thermogravimetric analysis (TGA) was performed on a NETZSCH STA 449C with a heating rate of 20 K/min under a nitrogen atmosphere (flow rate: 40 ml/min). 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 2θ range of 10 ° to 70 °. Scanning electronic microscope (SEM) images were obtained with a Philips XL-30.



(i) 3-(triethoxysilyl)-propyl isocyanate, reflux, pyridine, 70°C, 6h; (ii) TEOS, ethanol, rt, 4h; (iii) RE(NO₃)₃, TEOS, ethanol, rt, 4h

I



II

Scheme 1 I The procedures for the preparation of hybrid precursor and hybrid materials; II The hypothetic form mechanism of hybrid material I (a) and hybrid material II (b)

Results and discussion

The Fourier transform infrared (FTIR) spectra for 2,2'-dipyridylamine (a), the precursor (b), Hybrid material I (c) and Hybrid material II (d) are shown in Fig. 1. The peaks at 3247 cm⁻¹ in curve of 2,2'-dipyridylamine (a) is the unique vibration of NH group and it vanished when turned to the precursor (b) [24]. Two adjacent sharp peaks at 2,926 cm⁻¹ and 2,887 cm⁻¹ in curve of precursors (b) are $\nu_{as}(\text{CH}_2)$ and $\nu_s(\text{CH}_2)$ of the long carbon chain in precursors. And ¹H

NMR spectra relative to the precursors are in full agreement with the proposed structures. In the spectra of hybrid materials (I and II), the spectra are dominated by the $\nu(\text{Si}-\text{O}-\text{Si})$ absorption bands at 1,120–1,000 cm⁻¹. These indicated the formation of siloxane bonds. And residual silanol groups are evidenced by the $\nu(\text{Si}-\text{OH})$ stretching vibration at 900 cm⁻¹ [10]. The intensity decrease of other peaks may be due to the containing of the organic groups by the silicate inorganic host which occurred in the hydrolysis and condensation process.

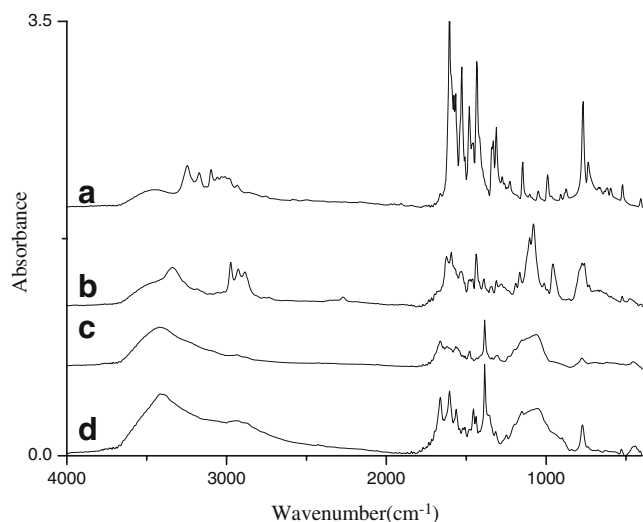


Fig. 1 Infrared spectra of 2,2'-dipyridylamine (a), the precursor (b), Hybrid material I (c) and Hybrid material II (d)

In spectrum of precursors (b), the ν (C=O) vibrations is located at $1,623\text{ cm}^{-1}$. As the ν (C=O) vibration is sensitive to the specificity and magnitude of hydrogen bonding, the intense component peak of hybrid material I (c) at $1,662\text{ cm}^{-1}$ corresponds to C=O groups included in much more ordered hydrogen-bonded aggregates (C = O \cdots H–N) [25]. In the spectrum of hybrid material II (d), the ν (C=O) vibrations is also shifted to the $1,662\text{ cm}^{-1}$. It suggests that the hydrogen-bonded aggregates also took place in hybrid material II. In the previous research, the compare between the infrared spectrum of a coordinated pyridine and that of the free base has been used to investigate the coordination process [26]. Two of the changes noted by these investigators are (1) a shift of the four principal bands of pyridine between $1,430$ and $1,600\text{ cm}^{-1}$ (which are due to ring C–C and C–N stretching vibrations) with the highest frequency band giving the largest shift, and (2) a shift of the ring breathing frequencies and C–H in-plane deformations, which occur in the 985 to $1,250\text{ cm}^{-1}$ region. The frequencies of the four principal bands found for 2,2'-dipyridylamine, the precursor, Hybrid material I and Hybrid material II in the region $1,410$ to $1,615\text{ cm}^{-1}$ are listed in Table 1. Two of these bands are attributable to symmetric and the other two to asymmetric in-plane ring deformations arising from the C–C and C–N stretching vibration.

Table 1 Assignments of the different of infrared absorption bands between 2,2'-dipyridylamine, the precursor and Hybrid materials (cm^{-1})

	ν (C=O)	C–C and C–N stretching			
2,2'-dipyridylamine		1,605	1,528	1,481	1,458
the precursor	1,623	1,594	1,531	1,479	1,459
Hybrid material I	1,662	1,619	1,565	1,479	1,461
Hybrid material II	1,662	1,605	1,563	1,454	1,439

Because of the domination of the ν (Si–O–Si) absorption bands at $1,120$ – $1,000\text{ cm}^{-1}$, the two lower frequency bands for these compounds in the 985 to $1,250\text{ cm}^{-1}$ region can not be clearly distinguished so they are not listed in Table 1. Comparison of these four bands from ring C–C and C–N stretching vibrations for the precursor and Hybrid material II shows that the bands shift, indicating that the pyridine group is coordinate to the metal ions. Comparison for the four bands for the precursor and Hybrid material I indicates slight shift in the first and second vibrations while the others keep constant. This mostly owing to the weak interactions between pyridine groups such as π – π staking when the hydrogen-bonded aggregates took place in hybrid material I.

Fluorescent whitening agents (FWAs) have characteristic absorptions in the range of 300 – 400 nm and emitting fluorescence located in the range of 400 – 500 nm . Figure 2 shows the diffuse reflectance ultraviolet-visible spectra (DRUVS) of hybrid material I (a) and hybrid material II (b). In the spectra, all hybrids exhibited broad absorption in the UV range. The ultraviolet absorbance rang enlargement for hybrid material II is owing to the enhancement of lanthanide ions coordinated to the pyridine groups.

On light absorption fluorescent whitening agents pass from the ground singled state S_0 to the excited state S_n . Figure 3 is the excitation spectra of hybrid material I (a) and hybrid material II (b) at 480 nm under room temperature. The spectra exhibits a broad excitation bands centered at 355 nm for hybrid I and 368 nm for hybrid II in the UV range, respectively. The increase of absorption peak at 368 nm is also attributed to the coordination of the lanthanide ions to pyridine groups. We choose the wavelength with maximum absorptions as the excited wavelength to explore their fluorescent properties.

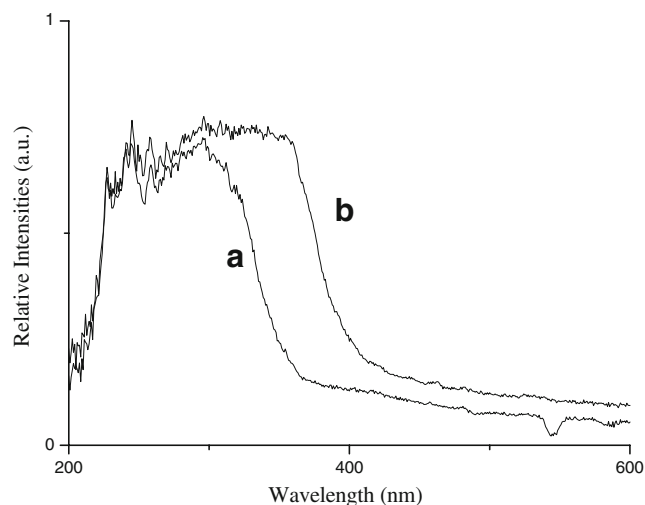


Fig. 2 Diffuse reflectance ultraviolet-visible spectra of hybrid material I (a) and hybrid material II (b)

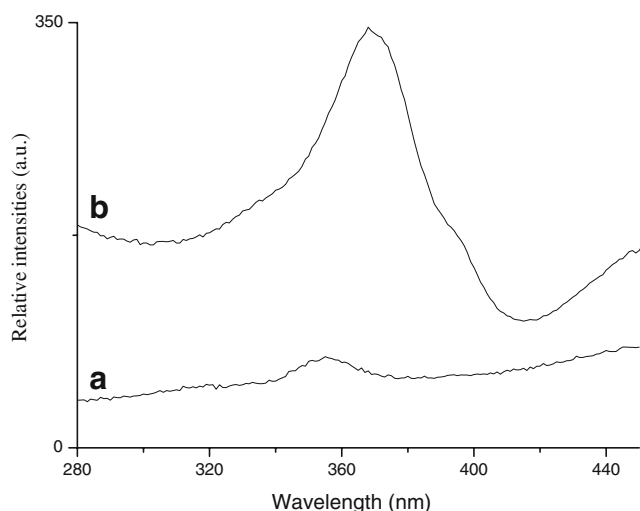


Fig. 3 The excitation spectra of hybrid material I (a) and hybrid material II (b)

The fluorescence behaviors of all of the hybrid materials have been investigated at 298 K by direct excitation of the ligands (368 nm). Fluorescent spectra of hybrid material I and four kinds of hybrid material II are given in Fig. 4. All of the spectra have similar curve profiles and broad absorption peaks are observed. Because no lanthanide ions are doped in them, hybrid materials I can only emit the fluorescence of the organic group. The peak of the emission is located at 400–450 nm. The spectrum of terbium doped hybrid materials (terbium hybrids for short) has a peak located at 406 nm. And the peak of the emission spectrum for the dysprosium hybrids, samarium hybrids, and europium hybrids is 410, 397–408 and 410 nm respectively. Between the spectra of hybrid material I and hybrid material II, half peak breadths of them also change. But those emissions are not the characteristic emission of the lanthanide ions. They are still the emission of the organic

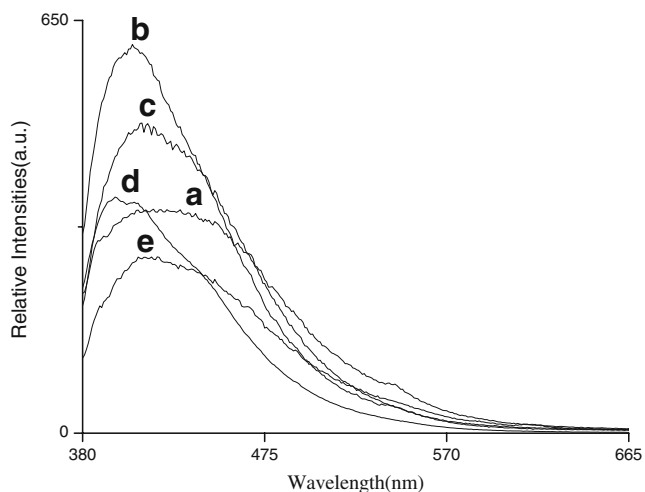


Fig. 4 The emission spectra of the hybrids I (a), terbium hybrids (b), dysprosium hybrids (c), samarium hybrids (d), europium hybrids (e)

groups but not the transition from excited singlet state to the ground state. The peak locations of four kinds of hybrid materials are different because the lanthanide ions' effects to pyridine rings are different.

An important parameter characterizing the organic group is the energy of the excited triplet state T. The energy of first excited triplet state E_{T1} was determined by the interaction of the phosphorescence spectra. The phosphorescence spectra of 2,2'-dipyridylamine was recorded in 77 K in Fig. 5. The curve exhibited a broad phosphorescence band located in 410–430 nm. Compare this data with the emission of the hybrid materials II, a conclusion could be drawn that the emission of the lanthanide ions doped hybrids is the transition from the excited triplet state of pyridine group to the ground state. Lanthanide ions take upon an evidently effect on the emission.

Thermal characterizations of fluorescent whitening agents were recorded and the TGA traces of 2,2'-dipyridylamine (a), Hybrid material I (b) and the Hybrid material II (c) are shown in Fig. 6. This represents hybrid material I and hybrid material II exhibit excellent thermal stability since all of their decomposition temperatures are larger than 2,2'-dipyridylamine and 200 °C, exceeding the operating temperature of pelletization in the industrial application [26].

The X-ray diffraction graphs of 2,2'-dipyridylamine (a), Hybrid material I (b) and Hybrid material II (c) and hybrid material I simply doped with Terbium nitrates (d) are showed in Fig. 7. In the spectrum of 2,2'-dipyridylamine (a), there are characteristic X-radiation peaks of 2,2'-dipyridylamine crystals. But the diffractogram of hybrid materials reveals that all of the hybrid materials with $10^\circ \leq \theta \leq 70^\circ$ are mostly amorphous. To Hybrid material I (b), it is dominated by a broad peak centered 22.49° and there are some narrow peaks protrude from the baseline which are attributed to the regular arrangement of the organic groups.

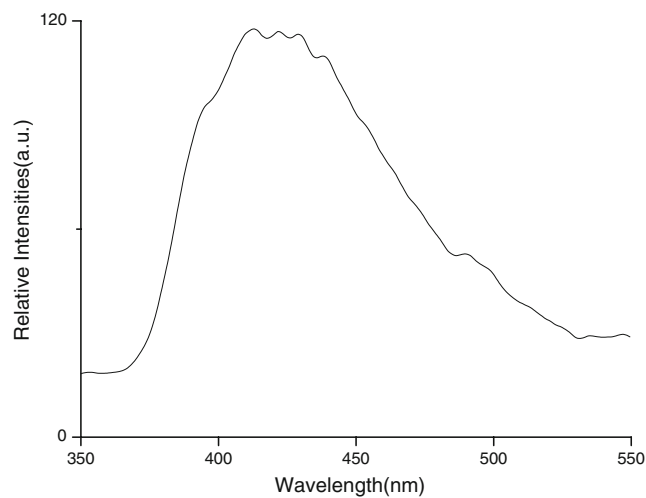


Fig. 5 Phosphorescence spectra of 2,2'-dipyridylamine

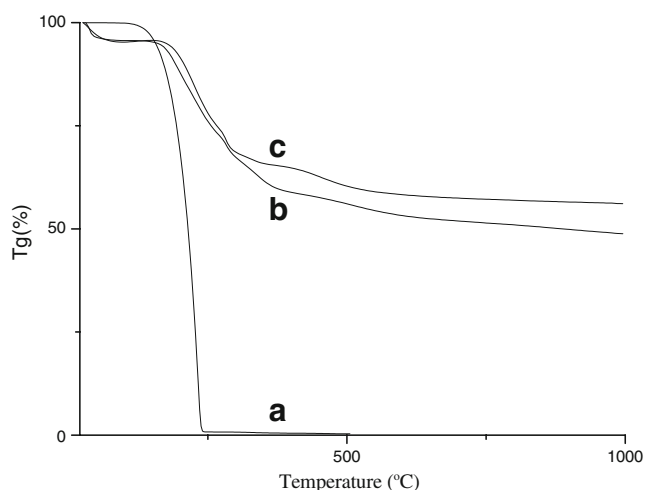


Fig. 6 The thermogravimetric analysis (TGA) trace of 2,2'-dipyridylamine (a), Hybrid material I (b) and Hybrid material II (c)

This is consistent with the suggestion of π - π stacking interactions between pyridine groups which was proved in this paper previously. However, there are totally amorphous in the Hybrid material II (c). To exclude the impact of lanthanide nitrates, hybrid material I simply doped with Terbium nitrates according to the ratio of previous experiment description are prepared and its XRD spectrum (d) is measured. Between (b) and (d), the major differences take place around 10^0 and the intensities of narrow peaks decrease which means that the peak for Terbium nitrates is located around 10° and simply mix could not lead to a total amorphous. Compare (c) with (d), peaks of Terbium nitrates and the narrow peaks appeared in (b) are all disappeared which means that the lanthanide ions are singly doped in the host other than Terbium nitrates and because of the coordination between lanthanide ions and the

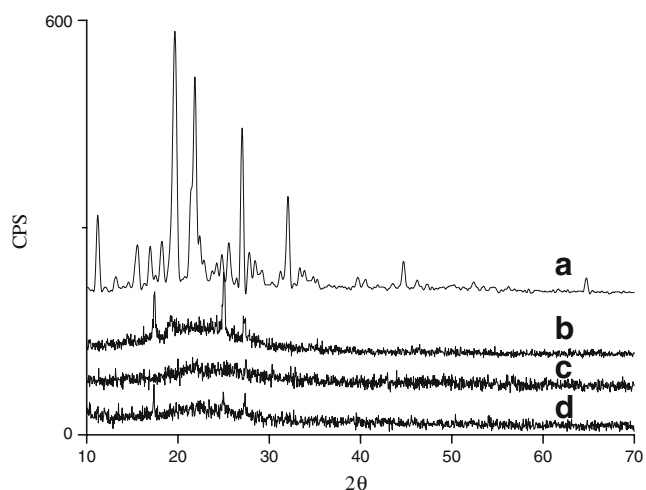


Fig. 7 The X-ray diffraction graphs of 2,2'-dipyridylamine (a), Hybrid material I (b) and Hybrid material II (c) and Hybrid material I doped with Terbium nitrates (d)

pyridine groups the regular arrangement of the organic groups in hybrid material I are disturbed.

The scanning electron micrographs (SEM) of these hybrid materials can give some proofs from the texture. Figure 8 demonstrates that micro-particle materials were obtained. Left graph is hybrid material I and right graph is hybrid material II. These are mostly owing to the adapting sol-gel treatment. In the sol process, the o/w macro-emulsion is decisive and responsibility for the materials' final texture. The difference between two hybrids is the scale of two kinds of particles and it can be resolved easily. In hybrid material I, because of the hydrogen-bond, organic groups aggregated and because of the weak interactions between the organic moieties such as van der Waals, London, or π - π staking, the organic moieties arranged regularly which was proved previously. For the bi-sphere particle, it may be supposed that pervasions take place between two spheres [see A in Scheme 1 (II)]. In the hybrid material II, the coordination between organic groups and lanthanide ions disturbed the regular arrangement of the organic moieties so the particle scale of the hybrid material

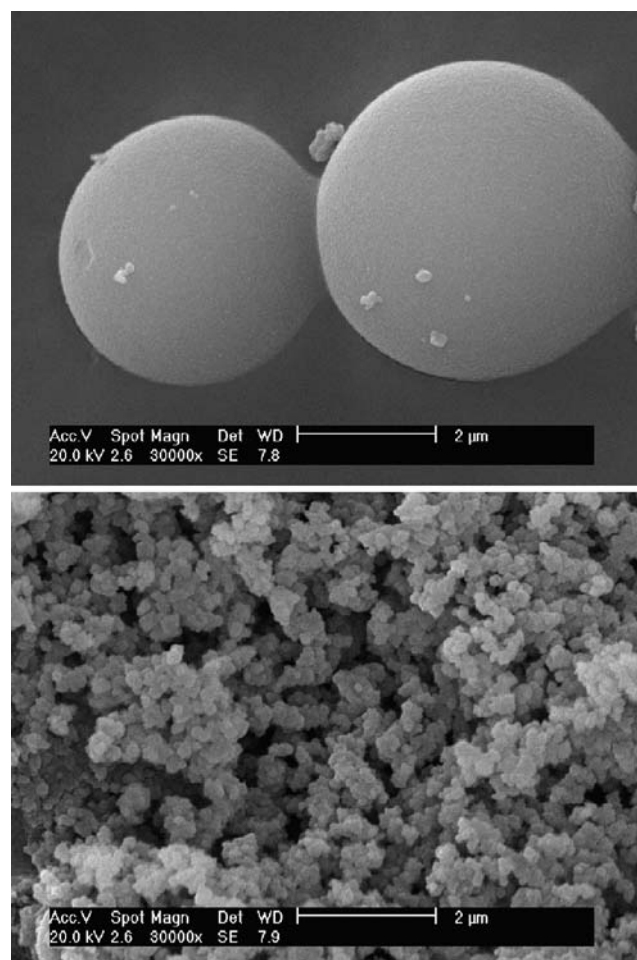


Fig. 8 The scanning electron micrographs of hybrid materials

II is smaller than that of the hybrid material I. And this hypothesis is drawn in Scheme 1 (II) (B).

Conclusions

In this work, a series of potential lanthanide activated fluorescent-whitening hybrid micro-particles has been prepared by an adapting traditional sol-gel method based on an o/w process and organosilane polycondensation. This result validates our previous assumption that the coordination between the ions and the ligands in the sol-gel process can impact on the organization in those amorphous systems. Although all the hybrid materials are amorphous, the organization does exist and could be adjusted. As far as particle internalization is concerned, experiments suggest that the coordination impacts largely on the texture of the final material. However, efforts are still needed to control the particle size dispersion, a key parameter for industry usage. In the case of whitening properties, these activated materials with lanthanide ions represent a novel way to produce fluorescent whitening agents.

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