



Interfacial self-assembly of bipyridyl-functionalized nanoSiO₂-BPy@Ln(β -diketone)_n composites and their luminescent properties



Yue-Yang Ma^a, Hong-Xiang Huang^b, Meng Chen^c, Dong-Jin Qian^{a,*}

^a Department of Chemistry, Fudan University, 220 Handan Road, Shanghai 200433, China

^b Department of Macromolecular Science, Fudan University, 220 Handan Road, Shanghai 200433, China

^c Department of Materials Science, Fudan University, 220 Handan Road, Shanghai 200433, China

ARTICLE INFO

Keywords:

Self-assembly
Nano-composite
Silica nanoparticle
Lanthanide complex
Luminescence

ABSTRACT

Interfacial self-assembly provides an effective route to design and construct various metal-organic hybrid and composite materials with interesting optical and electroactive properties. Here, we reported the interfacial self-assembly of luminescent nano-composites through the coordination reaction of lanthanide salts of Ln(CF₃SO₃)₃ (Ln = Eu and Tb) with the 2,2'-bipyridyl (BPy)-functionalized silica nano-linkers (nanoSiO₂-BPy) and several β -diketone ligands. The assembling processes and the nano-materials as-prepared were characterized by using thermogravimetry, infrared, UV-vis absorption and X-ray photoelectron spectroscopy, as well as field emission transmission electron microscopy (FE-TEM). The luminescent properties from both nanoSiO₂-BPy linkers and lanthanide nano-composites were investigated in the solutions and solid powders, which revealed not only the broad emissions of nanoSiO₂-BPy linkers between 400 and 520 nm, but also the sharp emissions between 480 and 750 nm, designated to the 4f-4f electron transitions of ⁵D₄ → ⁷F_n (n = 3,4,5,6) and ⁵D₀ → ⁷F_n (n = 0,1,2,3,4) of the Tb³⁺ and Eu³⁺ ions, respectively. The relative emission intensity of the Ln³⁺ ions in the nano-composites has been found to be closely dependent on the compositions of the nano-composites, structure of the β -diketone ligands, and the excited wavelengths. Finally, the energy transfer process in the nano-composites was discussed.

1. Introduction

Luminescent lanthanide (Ln) complexes have attracted much attention in the past several decades because of their unique luminescent properties and potential applications in many fields such as highly efficient photo-emitting materials [1–5], organic light emitting diodes [6,7], biomedical analyses and imaging [8,9], sensors for pH, oxygen and selected anions [10]. The Ln-complexes generally contain one or more light-harvesting units (ligands), such as organic acids, shift bases and β -diketones [1,3–5]; these ligands act as antenna to absorb light energy, then transfer the energy absorbed to the excited levels of the Ln (III) ions via an intersystem crossing process, and finally give off typical Ln(III) ion luminescent emissions [1–3]. The luminescent emissions of the Ln-complexes can cover the spectroscopic range (0.3–3 μ m) from ultraviolet to visible and near-infrared light (ultraviolet, blue, green, orange and red) only dependent on the types of the Ln(III) ions, that is, the energy gap between their ground and excited levels of 4f orbital electron. Because the 4f orbitals of Ln(III) ions are shielded by the filled 5s²5p⁶ sub-shells, such a structural feature endows the Ln(III) ions and their complexes with narrow-line emission bands, resulting in a strong

academic interest and wide range applications [3,7,9,11].

With the developments in supramolecular chemistry, molecular assembly, and nanoscale science and technology, the luminescent properties of Ln(III) complexes are not only investigated in the solutions as luminescent probes [12], but also widely done in the supramolecules, building blocks, organized thin films and nano-materials [13–16]. Earlier work on the interfacial assembly of organized thin films of the luminescent Ln(III) complexes has pointed out that the emission behaviors of Ln(III) ions are similar to those in their crystals due to a closely packed well-defined arrangement of the amphiphilic Ln(III) complexes in the thin films [17]. Later, to improve the film stability, several research groups have used the Ln-complex subphases and mixtures of the Ln(III) complexes with traditional amphiphilic molecules like arachidic acid [18–21]. As a result, it becomes possible to assemble ultrathin films of polynary Ln(III) complexes and to construct Ln-complex nano-materials with potential applications for light conversion devices, biological probes, gas sensors, as well as next-generation luminescent and magnetic materials. A very recent review has been done by Sharma and co-workers who summarized binary and ternary lanthanide complex nanophosphors for the photonic applications [22].

* Corresponding author.

E-mail address: djqian@fudan.edu.cn (D.-J. Qian).

<https://doi.org/10.1016/j.jlumin.2018.06.068>

Received 19 December 2017; Received in revised form 1 June 2018; Accepted 22 June 2018

Available online 23 June 2018

0022-2313/ © 2018 Elsevier B.V. All rights reserved.

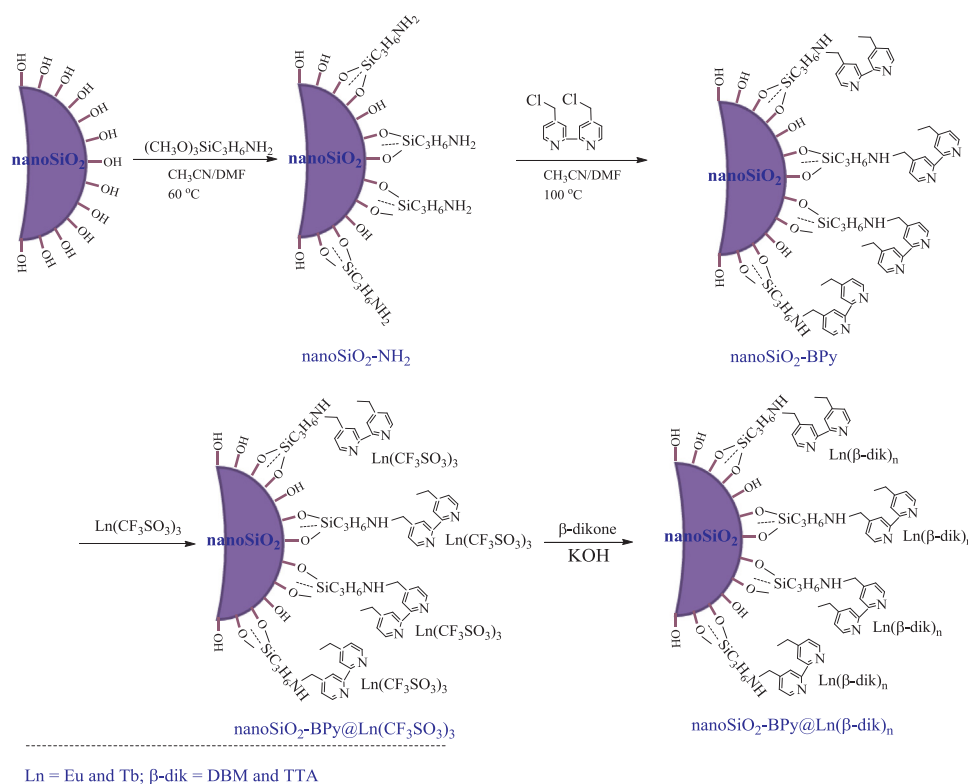


Fig. 1. Schematic representation for the preparation of the nanoSiO₂-NH₂ hybrids, nanoSiO₂-BPy linkers, nanoSiO₂-BPy@Ln(CF₃SO₃)₃ and nanoSiO₂-BPy@Ln(β -dik)_n composites.

When chiral ligands are used to coordinate with Ln(III) ions and acted as antenna, the lanthanide complex nano-hybrids, thin films or gels can produce circularly polarized luminescence and colored optical waveguides [23–25]. When multi-dentate ligands are used, various architectures can be constructed, such as polynuclear clusters, giant polyhedral cages or metal-organic frameworks that can be used for the metal ions' selection and luminescent fingerprint [26–28]. Further, when mixed lanthanide ions such as Tb(III) and Eu(III) are used to coordinate with ligands at different molar ratios, the as-produced materials can be used for the color-tunable luminescence, integration Boolean logic operation and luminescent logic gate mimics [29,30].

Besides the use of organic acids, shift bases and β -diketones as the ligands for the luminescent materials, the supramolecular thin films and nano-structural composites containing sandwich type Ln(III) complexes with the macrocycle ligands of phthalocyanines and porphyrins have been constructed for the air-stable organic field effect transistors [31,32]. The improved device stability and performance have been attributed to stronger molecular interactions such as hydrogen bonding and stacking interaction between two triple-decker macrocycles, as well as to minimize the steric hindrance between the basic building blocks and electrode surfaces.

The Ln(III) ions have high coordination requirements, thus, often allowing for the formation of coordination polymers and supramolecular systems such as bundles, grids, helicates and interlocked molecules [13]. These features further result in a possibility for an interfacial self-assembly to construct luminescent sensitive materials that allow for sensing on surface rather than the traditional solution based approach, and allow for the development of novel functional sensing devices [15,21]. Such kinds of direct coordination binding of Ln-complexes on the surfaces of inorganic materials are convenient routes for the construction of highly efficient fluorophore or emitters, which can be facilely used for the fabrication of luminescent devices and sensors, as well as for the biological probes of cells and tissues [9,16,33,34].

Here, we reported an interfacial self-assembly of luminescent Ln-

complex nano-composites through the coordination reaction of Ln(III) ions with the 2,2'-bipyridyl (BPy)-functionalized silica nano-linkers (nanoSiO₂-BPy). These nanoSiO₂-BPy linkers were prepared via the silanization and substitution reaction processes by using the hydrophilic nanoSiO₂ particles (diameter, ~ 12 nm) as the starting materials with excess 3-aminepropyltrimethoxysilane (APTMS) and 4,4'-bis(chloromethyl)-2,2'-bipyridyl (BPyCH₂Cl) [35,36]. The nanoSiO₂-BPy linkers were then used as the supports and multi-dentate ligands to coordinate with the Ln(CF₃SO₃)₃ salts to produce the nanoSiO₂-BPy@Ln(CF₃SO₃)₃ composites that were finally reacted with β -diketone (β -dik) ligands to produce the nanoSiO₂-BPy@Ln(β -dik)_x composites. The nano-materials as-produced were characterized by using thermogravimetry (TG), infrared, UV-vis absorption and X-ray photoelectron spectroscopy (XPS), as well as field emission transmission electron microscope (FE-TEM). The luminescent spectra of the nano-composites in the solutions and solid powders revealed a broad band between 400 and 520 nm designated to the nanoSiO₂-BPy linkers' emissions, and several sharp peaks between 480 and 750 nm, designated to the fluorescent emissions from the central Ln(III) ions. The relative emission intensity of the Ln(III) ions has been found to be closely dependent on the compositions of the nano-composites, structure of β -diketone ligands and the excited wavelengths.

2. Experimental section

2.1. Materials

Ludox AS40, obtained from Aldrich, was used as the starting silica material; it contained 40 wt% SiO₂, and had an average particle size of ~ 12 nm. APTMS, europium trifluoromethanesulfonate, and terbium trifluoromethanesulfonate were from Acros Organics. BPyCH₂Cl, thienyltrifluoroacetone (TTA), and dibenzoylmethane (DBM) were from Tokyo Chemical Industry Co., Ltd. The solvents were from Sinopharm Chemical Reagent Co. Ltd. All chemicals were used as received without

Download English Version:

<https://daneshyari.com/en/article/7839702>

Download Persian Version:

<https://daneshyari.com/article/7839702>

[Daneshyari.com](https://daneshyari.com)