

Molecular-based smart hybrid material through in situ sol–gel process: Artificial assembly of terbium with modified bridge ligand and luminescence

Li-Min Zhao, Bing Yan*

Department of Chemistry, Tongji University, Siping Road 1239, Shanghai 200092, China

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Abstract

A kind of functional monomer (abbreviated as BIMA-APMS) was synthesized by means of the amidation reaction of benzimidazole-5-carboxylic acid (BIMA) with a cross-linking molecule (3-aminopropyl)trimethoxysilane (APMS). Then, the composite materials were obtained by reaction of this kind of monomer (BIMA-APMS), tetraethoxysilane (TEOS) and $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ by an in situ sol–gel process, resulting in a novel molecular composite material (named as Tb-BIMA-APMS) with double chemical bonds (Tb–O coordination bond and Si–O covalent bond). Ultraviolet absorption, phosphorescence and fluorescence spectra were applied to characterize the photophysical properties of the obtained composite material. The strong luminescence of Tb^{3+} substantiates optimum energy match and effective intramolecular energy transfer between the triplet state energy of modified ligand bridge and emissive energy level of Tb^{3+} .

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1. Introduction

The field of inorganic–organic composite materials has evolved in recent years because functional composite materials not only combine the beneficial properties of the inorganic and organic components in a single material but also exhibit exceptional properties that exceed what would be expected for a simple mixture of the components [1]. Versatile applications for composite materials have expanded from their original base of enhanced mechanical properties and abrasion resistance. The current generation of materials is providing examples of novel optoelectronic [2], separation [3], catalytic [4], biological [5,6] and ion-conduction behavior [7,8]. The sol–gel reaction has been used in making inorganic–organic composite materials so far because of the advantages of the sol–gel technique such as the reaction condition of ambient temperature and high uniformity of inorganic parts in the silica matrix [9–11]. An important characteristic of inorganic–organic composite materials made by the

sol–gel reaction is the homogenous dispersion of the organic species at the molecular level into the inorganic networks [12]. As far as inorganic–organic composites are concerned, they can be divided in two major classes in terms of interactions between phases [13]. The first class is that the organic and inorganic phases are linked together with weak interactions such as hydrogen bonding, van der Waals force or weak static effect, which offers cohesion to the whole structure, namely, they are physically mixed; the latter is also biphasic material with difference that powerful covalent bonds link the organic and inorganic parts, i.e. they are chemically bonded [14–19]. The class II belongs to the molecular-based composite materials, which can realize the possibility of tailoring the complementary properties of novel multifunctional advanced materials through the combination with at chemical bonding within the different components in a single material [15,19–22].

The photophysical properties of rare earth ions are studied with a lot of interest because of their excellent luminescence characteristics from the electronic transitions between the 4f energy levels. They can be used as visible and near-IR radiation sources, some of them particularly important for solid-state lasers, scintillators field, optical communication amplifiers, and

* Corresponding author. Tel.: +86 21 65984663; fax: +86 21 65982287.
E-mail address: byan@tongji.edu.cn (B. Yan).

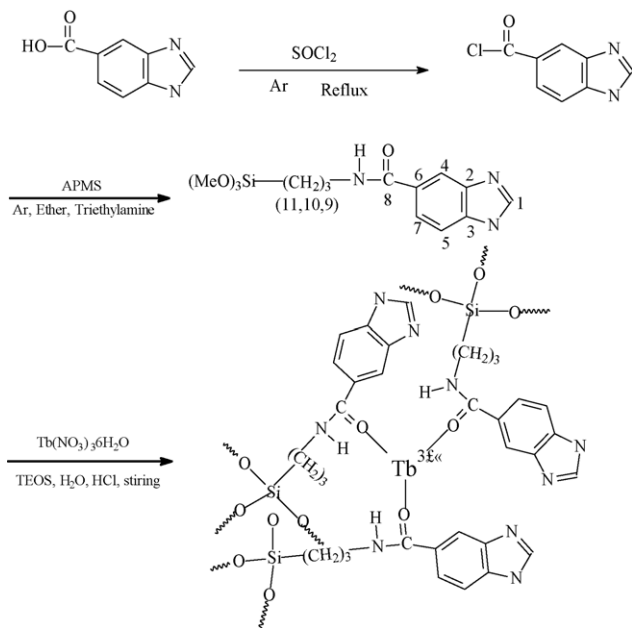


Fig. 1. Scheme of the synthesis process of BIMA-Si and predicted structure of composite materials.

the very large lamp market. In recent years, some work has been reported on the incorporation of lanthanide into the alkoxy silane modified by organic group to form the inorganic–organic composite material, which can modify the mechanic properties of matrix and material effectively and bear excellent luminescence characteristic [14,19,22–29].

This paper addresses the synthesis of a novel luminescent molecular-based terbium composite material by using modified benzimidazole-5-carboxylic acid (BIMA) as organic ligand, and utilizing the sol–gel reaction of tetraethoxysilane (TEOS) as previously published in our group [19–21]. FT-IR and NMR

have been used in order to study the structural of procedure; the photophysical properties were discussed in detail.

2. Experimental

Benzimidazole-5-carboxylic acid was supplied by Lancaster Synthesis Ltd. (3-aminopropyl)trimethoxysilane (abbreviated as APMS) was purchased from shanghai YaoHua chemical plant. Other starting reagents were used as received.

1.62 g (0.1 mol) BIMA was first converted to acyl chloride by refluxing in excess SOCl_2 under argon at 70°C in water bathing for 5 h. After isolation, the acyl chlorides were directly reacted with 1.79 g (0.1 mol) APMS in ethyl ether in presence of triethylamine. A typical procedure for the preparation of was according to reaction scheme in Fig. 1. BIMA-APMS (2.98 g) was received and yields were 92.3%. The date of ^1H NMR and ^{13}C NMR is as follows.

^1H NMR (DMSO): δ (ppm) 11.3 (1H,s) 8.46 (1H,s), 8.29 (1H,d), 7.91 (1H,d), 7.72 (1H,d), 6.8–7.2(1H,s) 3.56(9H,s), 2.25 (2H,t), 1.25 (2H,m), 0.75 (2H,t).

^{13}C NMR (DMSO): δ (ppm) 167.9 (C_8), 144.2 (C_1), 140.9 (C_3), 138.1 (C_2), 124.6 (C_6) 123.2 (C_7), 117.5 (C_4), 114.6 (C_5), 50.8 (C (OMe)), 35.6 (C_9), 23.2 (C_{10}), 13.9 (C_{11}).

A sol–gel derived composite material was prepared as follows: BIMA-APMS was dissolved in ethanol, and TEOS (tetraethoxysilane), H_2O were added while stirring, then one drop of diluted hydrochloric acid was put into it to promote hydrolysis. A stoichiometric amount of $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was added to the final stirring mixture. The mole ratio of $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ /BIMA-APMS/TEOS/ H_2O was 1:3:6:24. After the treatment of hydrolysis, 2 ml DMF (dimethylformamide) and appropriate amount of hexamethylene-tetramine were added to adjust the pH value of about 6.5. The mixture was stirred to achieve a single phase and thermal treatment was performed at 60°C until the sample solidified (see Fig. 2).

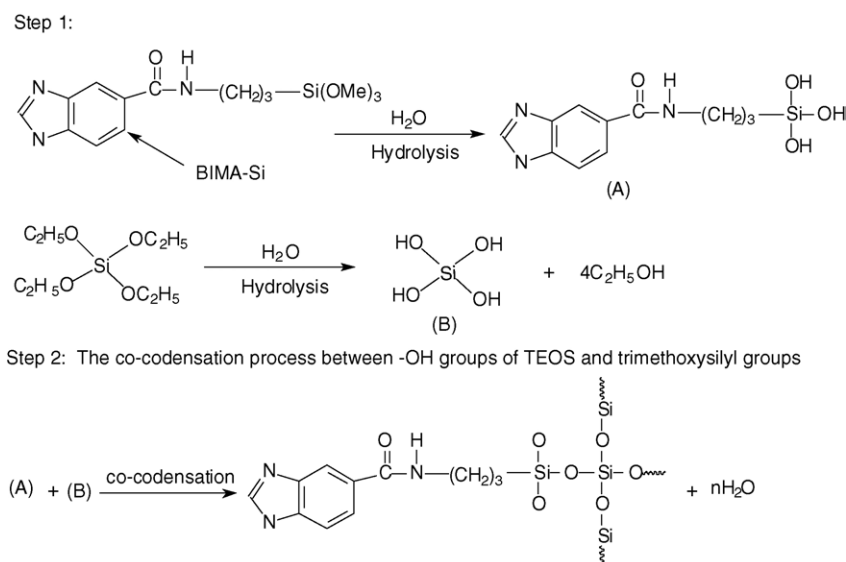


Fig. 2. Scheme of hydrolysis and polycondensation processes between BIMA-Si and TEOS.

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