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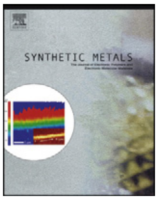

Photoactive ternary inorganic/organic hybrids of Al^{3+}, Zn^{2+} center/8-hydroxyquinoline functionalized Si–O network/polymer chain

Bing Yan*, Kai Sheng

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

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ABSTRACT

A novel series of metallic (Al, Zn) centered inorganic Si–O network/polymer hybrid materials have been constructed. Among functional linkage HQSi is achieved from the modification of 8-hydroxyquinoline (HQ) by 3-(triethoxysilyl)-propyl isocyanate (TESPIC) and used to covalently bonding Si–O network. Poly-(methyl methacrylate) (PMMA) or poly-(methacrylic acid) (PMAA) is introduced by the polymerization of methyl methacrylate (MMA) or methacrylic acid (MAA), respectively. Both inorganic Si–O network and polymer chain are coordinated to some metal ions (Al^{3+}, Zn^{2+}), resulting in the ternary luminescent hybrid material systems (abbreviated as HQ–Si–M–PMMA(PMAA), M = Al, Zn). The physical characterization and especially the photoluminescence property of them are studied in detail, which present the regular microstructure and green photoluminescence originated from the photoactive modified HQ functional unit by the perturbation of metallic ions (Al^{3+}, Zn^{2+}).

1. Introduction

In recently years, inorganic/organic hybrid materials have attracted great interest for they can easily integrate the special function of the organic and inorganic components [1,2]. The hybrid matrix may be polymer chain [3–5] or inorganic polymeric network [6,7], and composite host of inorganic/polymers [8,9]. Based on the interaction among the different components or phases in hybrid systems, these hybrid materials can be divided into two major classes [10]. The first is so-called physically mixed hybrids with weak interactions such as hydrogen bonding, van der Waals force or weak static effects between the organic and inorganic phases [6–9,11,12]; the second is named chemical bonded hybrids with covalent bonds linking the organic and inorganic parts [13–16]. The covalent bonds can be helpful to form the homogenous phase [10]. Among sol–gel technology is widely used to prepare hybrid materials because of its facility to produce adherent and crack-free silica materials [17,18]. We have realized six paths to modify organic ligands as functional bridge (linkage) to construct rare earth hybrid materials with chemical bonds: amino group modification [19], carboxyl group modification [20], hydroxyl group modification [21], merocapto group modification [22], sulfonic group modification [23], methylene modification [24]. After the modification, we assemble the above modified bridge ligands with rare earth ions and tetraethoxysilane (TEOS) to construct hybrid systems with chemical bonds [19–24].

On the basis of the above chemical bonded rare earth hybrids with Si–O inorganic polymeric networks, polymer chain can be further introduced to assembly the ternary rare earth/inorganic/polymeric hybrid materials with chemical bonds [25,26]. Many professional investigations have been focused on the rare earth hybrid materials containing inorganic and organic polymerization reactions and it is proved that these kinds of material can be expected to possess the more effective property, since each dispersed complex molecule is a luminescent unit so that the transparency, the dimension of the hybrids, the interfacial interaction between the rare earth luminescent species and the polymer matrices, and the dispersion of molecular degree are primary factors to determine the final luminescent behavior of the hybrids.

Aluminum 8-hydroxyquinoline (AlQ_3) is a stable metal chelated complex that can be sublimed to yield amorphous thin films and stands as the most widely used electron-transport host or emitting material for OLEDs [27]. Furthermore, crystallization takes place at the function time and results in a decrease in the work time. A convenient low-cost manufacturing method is solution processing, such as spin coating and possibly inkjet printing [28], with a mixture of 8-hydroxyquinoline (HQ) metal chelates and polymers [29]. However, in many cases phase separation occurs in these systems and leads to poor optical properties [29]. Covalently bonding the functional HQ metal chelates in inorganic matrix to form the hybrid material can improve the thermal stability and transparency of the chelates [21].

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

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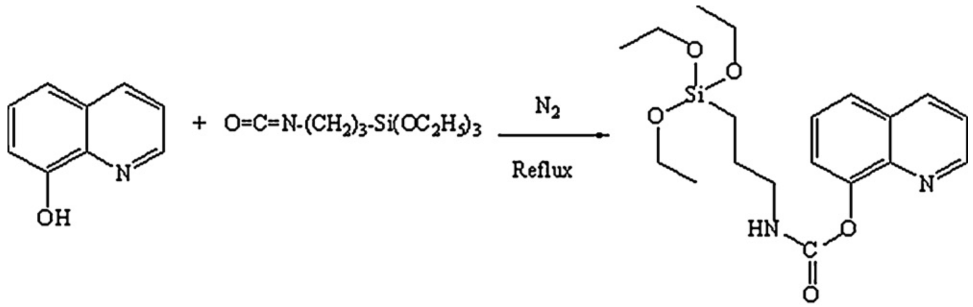
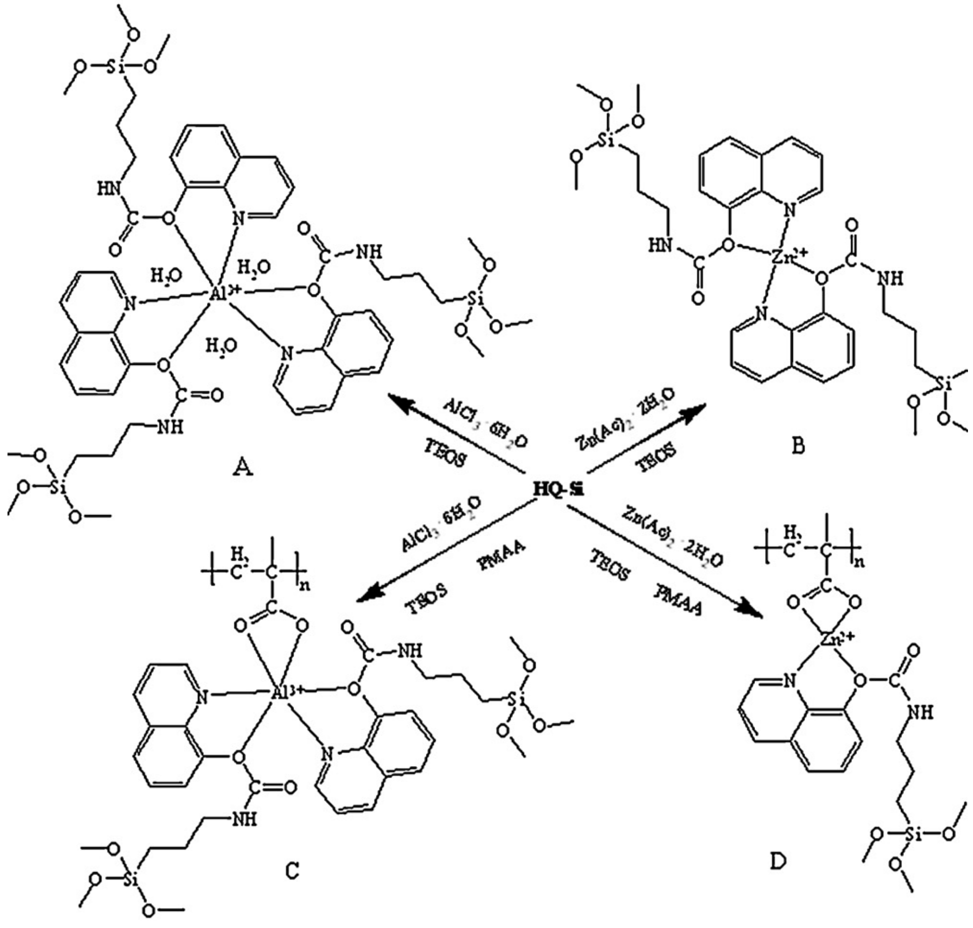


(I) Scheme of the synthesis process of the precursor HQSi



(II) Scheme of the predicted structure of the hybrids (A for Al-HQ-Si, B for Zn-HQ-Si, C for PMAA-Al-HQ-Si, D for PMAA-Zn-HQ-Si)

Fig. 1. Scheme of the synthesis process of the precursor HQSi (I) and the predicted structure of the hybrids (II) (A for Al–HQ–Si, B for Zn–HQ–Si, C for PMAA–Al–HQ–Si, D for PMAA–Zn–HQ–Si).

In this paper, on the basis of the novel kind of molecular precursor HQSi to design hybrids in our previous work [21], which is from the modification of organic compound 8-hydroxyquinoline by 3-(triethoxysilyl)propyl isocyanate (TESPIC). Two kinds of polymer chains, poly-(methyl methacrylate) (PMMA), poly-(methacrylic acid) (PMAA) are introduced into the above hybrid systems for the high coordination number of rare earth ions make it possible to assemble the multicomponent metallic (Al, Zn) center linking organically modified Si–O and polymeric chain. The detailed physical characterization and photoluminescence are discussed. For comparison, the binary (Al^{3+}, Zn^{3+}) hybrids are also prepared as ref. [21].

2. Experimental

2.1. Chemicals

TESPIC is provided by Lancaster Synthesis Ltd. The tetraethoxysilane (TEOS) is supplied by Aldrich. Methyl methacry-