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Improved photoluminescence properties of a novel europium(III) complex covalently grafted to organically modified silicates

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ABSTRACT

A series of novel organic–inorganic hybrid materials with a Eu(III) complex $[(C_2H_5)_4N][Eu(DBM)_3(DBM\text{-}OH)]$ (DBM = dibenzoylmethanate, DBM-OH = *p*-hydroxydibenzoylmethanate) covalently bonded into vinyl-modified silica networks have been successfully assembled through a sol–gel process. DBM-OH was grafted to the coupling agent 3-(triethoxysilyl)propylisocyanate (TESPIC), and the as-obtained molecular precursor DBM-Si was used as a bridge molecule both coordinate to Eu^{3+} and forming an inorganic Si–O network with tetraethoxysilane (TEOS) and vinyltriethoxysilane (VTES) after cohydrolysis and co-condensation processes. The luminescence properties of VTES/TEOS composite hybrid materials were systematically studied in comparison to those of TEOS-derived hybrid material and pure $[(C_2H_5)_4N][Eu(DBM)_4]$, respectively. The results indicate that the luminescent quantum efficiencies of VTES/TEOS composite hybrid materials are greatly improved. And it is interesting to find that the luminescent intensity of VTES/TEOS composite hybrid material is enhanced by optimizing the molar ratio of VTES to TEOS (VTES:TEOS = 4:6) by 3.3 and 2.4 times compared with TEOS-derived hybrid material and pure $[(C_2H_5)_4N][Eu(DBM)_4]$, respectively. In addition, the thermal stability of the emission was also improved considerably. The results presented in this paper indicate that the use of vinyl-modified silicates as a matrix opens the door to improving the photoluminescence properties of Eu(III) complexes.

1. Introduction

Rare-earth (RE) complexes are well known for their excellent luminescence properties, e.g., extremely sharp emission peaks, long lifetimes, and potential high internal quantum efficiency, which are due to effective intramolecular energy transfers from the coordinated ligands to the luminescent central lanthanide ions [1–3]. Some RE complexes demonstrate potential applications in fluoroimmunoassays, lasers, optical amplification, and organic light-emitting diodes [4–8]. However, their poor stability under high temperature and moisture and low mechanical strength restrict their practical applications.

A promising way to overcome these shortcomings is the use of the sol–gel method or the hydrothermal synthesis process to incorporate RE complexes into an inert matrix, such as inorganic and organic–inorganic hybrid matrices [9–16]. Organic–inorganic hybrid materials combine some advantages of organic compounds (easy processing with conventional techniques, elasticity, and organic functionalities) with properties of inorganic oxides (hardness, thermal and chemical stability, transparency); therefore they can exhibit excellent mechanical properties and good thermal and photostability [17–20]. Organically modified silicates (ORMOSILs) are one kind of organic–inorganic hybrid matrices with many excellent properties, such as low brittleness, considerable flexibility, and elasticity, with respect to traditional silica xerogels, and exhibit tremendous potential applications in optics, electrics, biology, and catalysis [21–24]. A typical process for preparing ORMOSILs is cohydrolysis and co-condensation from a mixture of a tetralkoxysilane and an alkyl-substituted silicon alkoxides. The nonreactive organic groups do not undergo hydrolysis or condensation, remaining unaltered during the sol–gel process and acting as a network modifier that terminates the silicate networks. Because the interconnection of organic and inorganic moieties in this network results in microstructure changes, improvement of density, flexibility, and optical properties has been achieved, making ORMOSILs more suitable as matrices for a range of applications. Recently, the use of ORMOSILs as a support has been of widespread interest in optical oxygen sensors [25–29]. However, only limited examples of using vinyl-modified silicates as matrices for Eu(III) complexes have been reported [30–32], and these studies were mainly focused on vinyl-modified silicate

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matrices doped with the Eu(III) complexes in which only weak physical interactions exist between the Eu(III) complexes and the matrices. Up to date, as far as we know, the synthesis and luminescence properties of vinyl-modified silicate matrices covalently bonded with Eu(III) complexes have not been explored.

Here, we report on the synthesis of a series of organic–inorganic hybrid materials covalently bonded with a novel Eu(III) complex $[(C_2H_5)_4N][Eu(DBM)_3(DBM\text{-}Si)]$ (depicted in Fig. 1) by a sol–gel process using ORMOSILs as matrices, in which VTES was selected as an organic modifier in the precursor. It is interesting that the luminescent intensity and emission quantum efficiency of these VTES/TEOS composite hybrid materials showed strong dependence on the molar ratio of VTES to TEOS. The luminescent intensity of VTES/TEOS composite hybrid material is enhanced by optimizing the molar ratio of VTES to TEOS (VTES:TEOS = 4:6) by 3.3 and 2.4 times compared with TEOS-derived hybrid material and pure $[(C_2H_5)_4N][Eu(DBM)_4]$, respectively. In addition, the thermal stability of the emission is also improved considerably.

2. Materials and methods

2.1. Materials

Tetraethoxysilane (TEOS, Tianjin Chemicals Co.), 3-(triethoxysilyl)-propyl isocyanate (TESPIC, Aldrich), vinyltriethoxysilane (VTES, Tianjin Chemicals Co.), acetophenone (Tianjin Chemicals Co.), *p*-hydroxybennic acid (Tianjin Chemicals Co.), tetraethylammonium bromide (Tianjin Chemicals Co.), and dibenzoylmethane (DBM, Aldrich) were used as received. The solvent tetrahydrofuran (THF) was used after desiccation with anhydrous calcium chloride. Europium chloride ($EuCl_3$) was prepared by dissolving Eu_2O_3 in concentrated hydrochloric acid (HCl).

2.2. Synthetic procedures

2.2.1. Synthesis of p-hydroxydibenzoylmethane (DBM-OH)

DBM-OH was prepared using a Claisen condensation between *p*-hydroxybenzoate and acetophenone in the presence of sodium

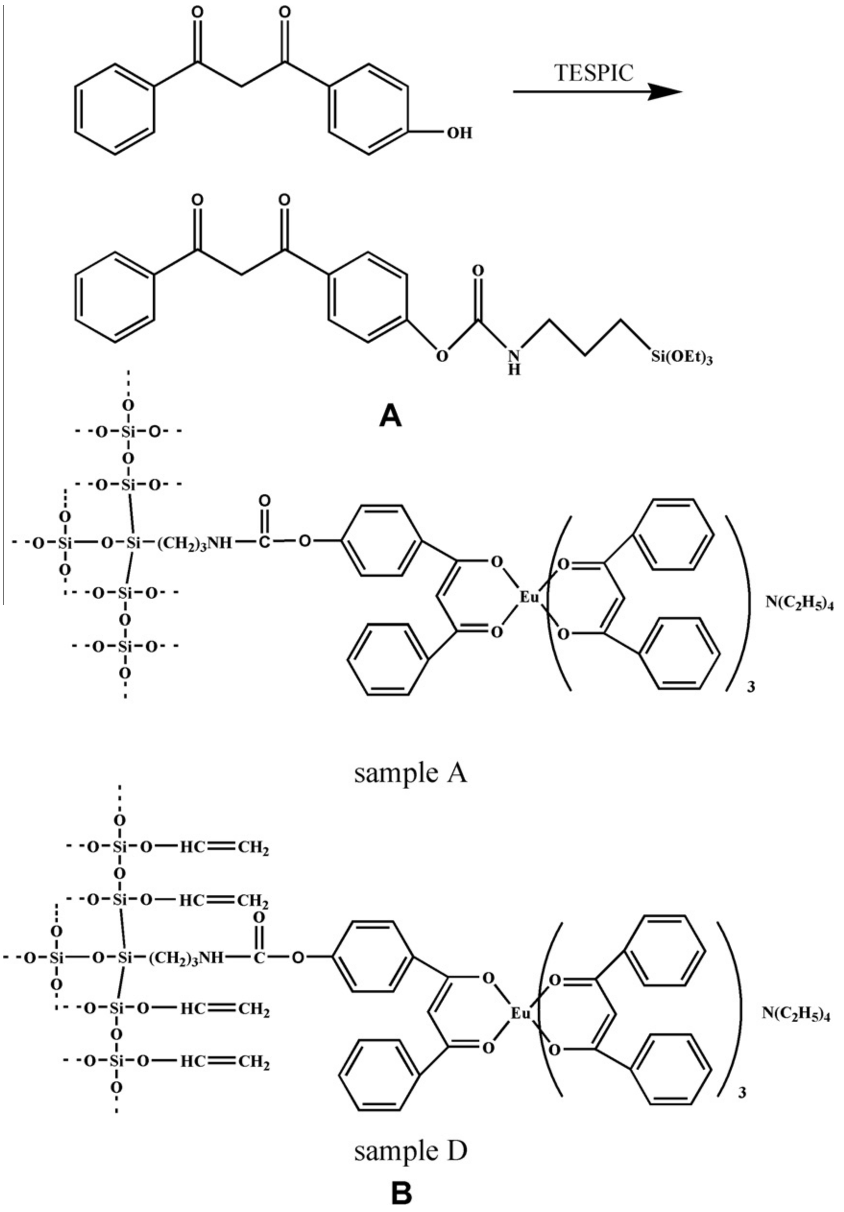

Fig. 1. Synthetic procedures of the silylated precursor DBM-Si(A) and the predicted structure of xerogels containing Eu(III) complex.