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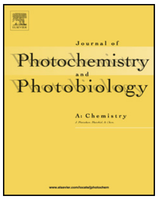

Soft materials composed with lanthanide (Eu^{3+}, Tb^{3+}) beta-diketonates and ZnO nanoparticles through ionic liquid linkage to integrate white luminescence

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ABSTRACT

In this note, 3-(2-(2-mercaptoacetoxy)ethyl)-1-methyl-1H-imidazol-3-ium bromide (SH-IL), a kind of room temperature thiol-functionalized ionic liquid compound is synthesized and used to interact with ZnO nanoparticles for the chemical affinity between S of SH-IL and Zn of ZnO. And then an anion exchange reaction is performed to introduce europium(III) and terbium(III) tetrakis β-diketonates (thenoyltrifluoroacetonate (TTA) or acetylacetonate (AcAc)) to ILs functionalized ZnO matrices. Subsequently, novel series of photoactive composites are assembled with ZnO nanoparticles and lanthanide complexes through SH-IL as bridge. Especially, it is worthy point out that the integration to white luminescence can be realized for the composite systems by adjusting the ratio of different active building units (red color for Eu complex, green color for Tb complex and blue color for ZnO unit). This result provides useful data to develop white-luminescent composite phosphors.

1. Introduction

Luminescent inorganic–organic composite materials have attracted considerable attention due to their extraordinary photostablity, which can be expected to have practical applications in luminescent devices and biosensor or bioimaging [1,2]. The combination of organic and inorganic components at a molecular or nanometer scale integrates certain advantages of organic unit (easy processing with conventional techniques, elasticity, and organic functionalities) and inorganic components (hardness, thermal and chemical stability) [3,4]. Among the most popular composites are based the special covalent linkage named organically modified silanes (ORMOSILs), which is to graft a typical photoactive organic ligand for lanthanide ions onto a special functional silane crosslinking reagent [5–10]. On the basis of lanthanide sol–gel-derived composite materials with ORMOSILs, it is natural to attempt further assembly of lanthanide mesoporous silica composites by grafting lanthanide complex units with templates [11–16]. Furtherly, organic polymer can be introduced into lanthanide composite system with coordination bond and covalent bond [17–20].

Previous research has shown that the key procedure in constructing these chemically bonded composite materials is to design the functional bridging molecule (ligand) by grafting, in which the bridging molecule behaves as a chemical linkage both coordinating and sensitizing lanthanide ions, as well forming covalent Si—O networks [3–10]. Here the main interaction is covalent bonding with host and coordination bonding with lanthanide ions. Besides, the ion exchange can also achieve the linking of lanthanide species and other functional component or host [21–24]. Among room temperature ionic liquid compounds (RTILs) are the good choice to the topic, whose salts consist of anion organic and cations. They are stabilized by ionic interaction through hydrogen bonds and van der Waals forces [25–27]. Many research uses the feature of ILs (can link the rest of the group) to synthesize functionalized ionic liquid compounds [28–30]. Moreover, some functionalized ILs can be expected to have potential to assemble composites for their reactive groups, such as carboxylic acid-, amino- and thiol-functionalized ionic liquid, etc. [31–35]. Recently, much work has been done focused on luminescent lanthanide β-diketonate complexes doped ionic liquids, which shows favorable luminescent performance like high quantum yield and stationary photo-stability [36–39].

However, the non-crystalline nature of the composite materials makes it difficult to determine their exact structures. So, the focus has shifted to the introduction of crystalline building blocks into composite systems to combine inorganic–organic composite, which favors them the luminescence behaviors of both inorganic phosphors and molecular materials [40–44]. In addition, the

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luminescence integration of the building units in the multi-component lanthanide composites is expected to realize the adjustable luminescence color and especially to emit white luminescence [45–47]. In our previous work, we have realized the multi-component assembly lanthanide complexes and metal sulfides through thiol-group derived liquid compounds [39].

In this work, we try to explore the possibility of luminescent composite materials with lanthanide complexes and functional oxide such as ZnO with 3-(2-(2-mercaptoacetoxy)ethyl)-1-methyl-1H-imidazol-3-ium bromide (SH-IL) as functional linkage or bridge (Yield: 85%. ^{1}H NMR δ (ppm in D-DMSO): 9.22(s 1H), 7.78(s 1H), 7.75(s 1H), 4.23(t 2H), 3.83(s 3H), 3.70(t 2H)). Lanthanide β-diketonates (thenoyltrifluoroacetonate (TTA) or acetylacetonate (AcAc)) complexes (Elemental analysis data: for $Eu(TTA)_4Na$ (1059.6592), Eu 14.50 (14.34), C 36.41 (36.27), H 1.40 (1.52); for $Tb(AcAc)_4Na$ (578.3466), Tb 27.61 (27.48), C 41.76 (41.54), H 4.70 (4.88)) and ZnO nanoparticles are assembled into one composite system for the multi-function of SH-IL. The photoluminescence, especially the white luminescence integration is discussed in detail.

2. Results and discussion

Ion liquid compound with —SH group such as SH-IL has the ability to link semiconductor for the affinity between S and metal component of semiconductor [39]. So SH-IL can be used as effective medium to disperse II–VI group semiconductor. Meanwhile, it can as well interact with lanthanide complexes through the ion exchange. Under this strategy, we disperse $Eu(TTA)_4{}^-$, $Tb(AcAc)_4{}^-$ and ZnO to SH-IL to construct multi-component composite material system. In a typical experiment, the amount SH-IL is kept the same (2 g), and $Eu(TTA)_4{}^-$, $Tb(AcAc)_4{}^-$ and ZnO with different molar ratio, which are named as ZnO-SH-IL-EuX (X = 2.5 and 5.0) and ZnO-SH-IL-EuX-TbY (x = 2.5, Y = 1), respectively. The reaction temperature is 70 °C for the assembly of composite. The contents of Eu^{3+}, Tb^{3+} ions and Zn^{2+} in the composites were determined with ICP-OES. For ZnO-SH-IL-Eu1.5: Eu 0.22 %, Zn 4.01; for ZnO-SH-IL-Eu2.5: Eu.0.37 %, Zn 3.90; ZnO-SH-IL-Eu5.0: Eu 0.77 %, Zn 3.78; for ZnO-SH-IL-Eu2.5-Tb1: Eu 0.35 %, Tb 0.16 %, Zn 3.93. Fig. 1 shows the scheme for the composition of the whole composite systems and experimental details can be seen in supporting information.

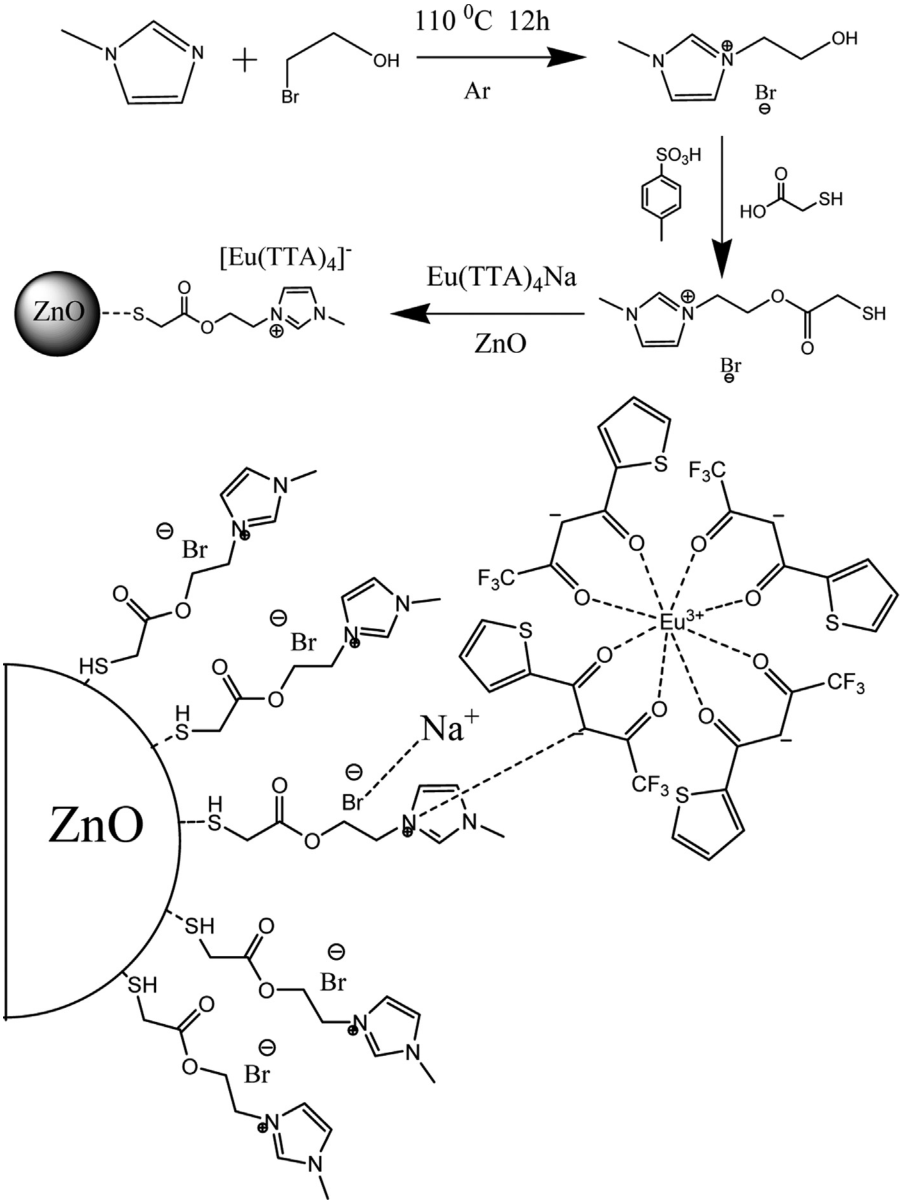

Fig. 1. The scheme for the composition of multi-component composites.