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Hybrid materials of MCM-41 functionalized by lanthanide (Tb^{3+}, Eu^{3+}) complexes of modified *meta*-methylbenzoic acid: Covalently bonded assembly and photoluminescence

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Abstract

Novel organic–inorganic mesoporous hybrid materials were synthesized by linking lanthanide (Tb^{3+}, Eu^{3+}) complexes to the mesoporous MCM-41 through the modified *meta*-methylbenzoic acid (MMBA-Si) using co-condensation method in the presence of the cetyltrimethylammonium bromide (CTAB) surfactant as template. The luminescence properties of these resulting materials (denoted as *Ln*-MMBA-MCM-41, *Ln* = Tb, Eu) were characterized in detail, and the results reveal that luminescent mesoporous materials have high surface area, uniformity in the ordered mesoporous structure. Moreover, the mesoporous material covalently bonded Tb^{3+} complex (Tb-MMBA-MCM-41) exhibits the stronger characteristic emission of Tb^{3+} and longer lifetime than Eu-MMBA-MCM-41 due to the triplet state energy of organic legend MMBA-Si matches with the emissive energy level of Tb^{3+} very well.

Keywords: Covalently bonded mesoporous host; Hybrid material; Lanthanide complex; Luminescence

1. Introduction

Luminescent materials, especially lanthanide phosphors, are applied in many devices of importance [1]. The interest in the photophysical properties of lanthanide complexes which act as optical centers in luminescent hybrid materials has grown considerably since Lehn [2] asserted that such complexes could be seen as light harvest supramolecular devices. Particularly, the design of efficient lanthanide complexes has acquired the attention of many research groups, focusing on the diverse classes of ligands, β-diketones, heterobiaryl ligands, etc. Our research group is focusing on the lanthanide complexes with aromatic carboxylic acid components, bipyridyl or their derivatives [3–5]. In the recent decades, the sol–gel technology has been frequently employed in the synthesis of a significant number of unique attractive organic–inorganic hybrid materials with delicate control and a wide scope of practical applications [6–9]. Consequently, hybrid silicate materials derived from organo-bridged silsesquioxane precursors with molecular scale homogeneity have now been considerably fabricated by this room temperature method. According to the chemical nature or different synergy between components, hybrids can be categorized into two main classes. The first class concerns all systems where no covalent bond is present between organic and inorganic parts but only weak interactions (such as hydrogen bonding, van der waals force or electrostatic forces). The corresponding conventional doping methods seem hard to prohibit the problem of quenching effect on luminescent centers due to the high vibration energy of the surrounding hydroxyl groups. Therefore, another attracting possibility with regard to the complexation of lanthanide ions using ligands that are covalently fixed to the inorganic networks has emerged. To date, few studies in terms of covalently bonded hybrids with increasing chemical stability have appeared and the as-derived molecular-based materials exhibit monophasic appearance even at a high concentration of lanthanide complexes

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[10–17]. Recently, our group has developed some types of covalently bonded hybrid materials by modifying aromatic acid with modified methyl, carboxyl or hydroxyl groups [18–20] as "molecular bridges". These bridges cannot only develop chelating effects that can bind to lanthanide ions but also link to a silica host with a methylalkoxysilane group.

Due to its peculiar characteristics, large internal surface area and favorable uniformity and easily controlled size of the pore, the ordered mesoporous molecular sieve MCM-41 has attracted considerable interest in physics, chemistry, materials science and other relevant areas [21]. There are many reports on the modification of inorganic mesoporous materials such as MCM-41 silica via post-grafting [22,23] or direct condensing of tetraalkoxysilanes (or organo-functionalized trialkoxysilanes) [24,25], which is also referred to as one-pot synthesis. The latter approach to synthesize MCM-41 was preferred by most researchers because of the simple single-pot synthetic protocol and easy control of organosilane distribution [26]. Besides the advantages of very high surface area, large pore volume and outstanding thermal stabilities, there are a large number of hydroxyl groups in MCM-41, which provide necessary qualification for the modification of inner face and self-assembly of huge guest molecules, namely, providing outstanding hosts for self-aggregation chemistry. Many research efforts, which have focused on preparing the organic/inorganic hybrids through the functionalization of the exterior and/or interior surfaces, prompted the utilization of MCM-41 in many areas [27–30].

Herein, we report a direct synthesis of *meta*-methylbenzoic acid (MMBA)-functionalized MCM-41 mesoporous hybrid material (MMBA-MCM-41), in which MMBA was covalently bonded to the framework of MCM-41 by co-condensation of the modified MMBA (denoted as MMBA-Si) and the tetraethoxysilane (TEOS) using the cetyltrimethylammonium bromide (CTAB) surfactant as template. The luminescent lanthanide (Tb^{3+}, Eu^{3+}) complexes on functionalized MCM-41 with modified MMBA (denoted as *Ln*-MMBA-MCM-41, *Ln* = Tb, Eu) were obtained by introducing Ln^{3+} into the MMBA-MCM-41 hybrid material. Thus, the lanthanide complex *Ln*(MMBA)$_3$ was successfully linked to the framework of MCM-41 via a covalently bonded MMBA group. Full characterization and detail studies of luminescence properties of all these synthesized materials were investigated in relation to guest–host interactions between the organic complex and the silica matrix.

2. Experimental

2.1. Materials

CTAB (Aldrich), TEOS (Aldrich), 3-(methylpropyl)-triethoxysilane (APES, Lancaster), MMBA, and ethanol were used as received. The solvent ether (Et_2O) was used after desiccation with anhydrous calcium chloride.

LnCl_3 (*Ln* = Tb, Eu) ethanol solution (EtOH) was prepared as follows: the rare-earth oxide (Tb_4O_7, Eu_2O_3) was dissolved in concentrated hydrochloric acid (HCl), and the surplus HCl was removed by evaporation. The residue was dissolved with anhydrous ethanol. The concentration of the rare-earth ion was measured by titration with a standard ethylenediamine tetraacetic acid (EDTA) aqueous solution.

2.2. Synthetic procedures

2.2.1. Synthesis of MMBA-functionalized MCM-41 mesoporous material (MMBA-MCM-41)

The MMBA-Si was prepared as follows: MMBA (1 mmol, 0.136 g) was first converted to acyl chloride by refluxing in excess $SOCl_2$ at the nitrogen atmosphere for 4–5 h. After isolation, the acyl chloride was directly reacted with 3-(methylpropyl)-triethoxysilane (APES) (1 mmol, 0.221 g) in ethyl ether in presence of triethylamine. The mixture was heated at 65 °C in a covered flask for approximately 12 h at the nitrogen atmosphere. After isolation and purification, a yellow oil sample MMBA-Si was obtained. Anal: calcd. for $C_{17}H_{29}NO_4Si$: C: 60.17; H: 8.55; N: 4.13; Found: C, 60.12; H, 8.49; N, 4.11%. ^1H NMR ($CDCl_3$): δ 7.78(1H, s), 7.76(1H,s), 7.41(2H,s), 3.80(1H,t), 3.45(10H,m), 3.10(2H,s), 2.33(3H,d), 1.57(4H,s), 1.19(2H,s), 0.59(3H,s). ^{13}C NMR ($CDCl_3$): δ 167.3(C_7), 137.6(C_1), 133.7(C_3), 130.6(C_6), 129.4(C_4), 128.4(C_5), 126.2(C_2), 72.5–71.4(C_9–C_{10}), 69.9(C_{11}), 55.9(C_8), 49.8(C_{12}), 18.4(C_{13}).

The mesoporous material MMBA-MCM-41 was synthesized as follows: CTAB (1.1 g) was dissolved in concentrated $NH_3 \cdot H_2O$ (12 mL), to which deionized water (26 mL), TEOS (5.5 mL), and MMBA-Si were added with the following molar composition: 0.12 CTAB:0.5 $NH_3 \cdot H_2O$:0.96 TEOS:0.04 MMBA-Si:58.24 H_2O. The mixture was stirred at room temperature for 24 h and transferred into a Teflon bottle sealed in an autoclave, which was then heated at 100 °C for 48 h. Then the solid product was filtrated, washed thoroughly with deionized water, and air-dried for 12 h at room temperature. Removal of the surfactant CTAB was conducted by Soxhlet extraction with ethanol for 2 days to give the sample denoted as MMBA-MCM-41.

2.2.2. Synthesis of MCM-41 mesoporous material covalently bonded with the lanthanide (Ln^{3+}) complexes (denoted as Ln-MMBA-MCM-41, Ln=Tb, Eu)

The sol–gel-derived mesoporous hybrid material was prepared as follows: while being stirred, MMBA-MCM-41 was soaked in an appropriate amount of *Ln*Cl_3 ethanol solution with the molar ratio of Ln^{3+}: MMBA-Si being 1:3. The mixture was heated at 75 °C under reflux for 12 h, followed by filtration and extensive washing with EtOH. The resulting materials *Ln*-MMBA-MCM-41(Eu^{3+}, Tb^{3+}) was dried at 60 °C under vacuum overnight and the lanthanide ion content of the materials was 1.26% (mol%). The hybrid mesoporous *Ln*-MMBA-MCM-41 product was obtained (as outlined in Fig. 1).