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Luminescent inorganic–organic hybrid films based on europium-substituted heteropolymolybdate and poly(amidoamine) dendrimer

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ABSTRACT

Multilayer films consisting of poly(amidoamine) (PAMAM) dendrimer and europium-substituted heteropolymolybdate $K_{17}[Eu(P_2Mo_{17}O_{61})_2]$ (simplified as $Eu(P_2Mo_{17})_2$) were prepared by layer-by-layer (LBL) self-assembly and characterized by UV–vis measurements, X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). UV–vis showed that the characteristic absorbance values of the multilayer films increased linearly with the layer numbers of $Eu(P_2Mo_{17})_2$/PAMAM films. The electrostatic interaction between $Eu(P_2Mo_{17})_2$ and PAMAM was demonstrated by XPS. In addition, AFM provided the surface morphology of $Eu(P_2Mo_{17})_2$/PAMAM films, revealing that the films contained well-defined $Eu(P_2Mo_{17})_2$ nanoparticles. The luminescence behavior of the films at room temperature was also investigated. The films exhibited the characteristic emission bands of Eu^{3+} and the fluorescence lifetime of Eu^{3+} in the films is shorter than that in the solid.

1. Introduction

Hybrid inorganic–organic materials are drawing great attention because they possess not only the stable and elegant optical, electric, and magnetic properties of the inorganic components but also the structural flexibility of organic chromophores [1,2]. The construction of such inorganic–organic hybrids is considered useful in obtaining multifunctional materials with new and desired electrical and optical properties [3,4]. An influential domain in the use of noncovalent interactions in hybrid-film research is electrostatic layer-by-layer (LBL) assembly, which offers the opportunity to create inorganic–organic hybrid film materials with well-defined structure and thickness, controlled at a molecular level [5,6]. The popularity of the method is due to its easy preparation and accurate control over wall thickness as well as flexibility in the choice of constituents [7].

Dendrimers are molecular architectures that provide an enormous opportunity to create new functional materials [8]. Their highly branched, globular architectures give rise to a number of interesting properties that contrast with those of linear polymers. Poly(amidoamine) (PAMAM) dendrimers have been demonstrated as suitable organized layers to LBL formation in studies of electrocatalysts on gold electrodes [9,10]. Polyoxometalates (POMs) are typical inorganic metal oxide clusters with a wealth of topologies and optical, electrical, and magnetic properties and are widely investigated in various fields such as catalysis, biology, medicine, and materials science [11]. Among these, rare earth metal-substituted POMs have won much attention due to their good luminescence characteristics and have been regarded as one of the best building blocks for the fabrication of functional hybrid materials [12–16]. Several reports have shown that the LBL method is also adaptable for the preparation of ultrathin inorganic–organic composite films from a cationic polymer and negatively charged POMs containing rare-earth ions [17,18]. However, these reports focus mainly on the fabrication of related multilayers with chain polymer, while the study on globular polymer is rarely reported.

In this study, the LBL deposition of oppositely charged species was used to fabricate multilayer films constructed from the negative sandwiched europium-substituted heteropolyoxometalates $[Eu(P_2Mo_{17}O_{61})_2]^{17-}$ (Fig. 1) and the positive protonated Generation-4 polyamidoamine (G4-PAMAM, Fig. 2) with globular shape. G4-PAMAM molecule has 32 surface amine groups that can be positively charged by protonation under acidic conditions. Furthermore, the luminescence properties of the films were studied with respect to the corresponding POM solid. To the best of our knowledge, LBL self-assembly of rare earth metal sandwiched POM and globular organic dendrimer in forming luminescent multilayer films has not been reported previously.

2. Experiments

2.1. Materials

All chemicals were of analytical grade and used as received unless otherwise stated. $K_{17}[Eu(P_2Mo_{17}O_{61})_2]$ $(Eu(P_2Mo_{17}))_2$ was

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prepared by a published procedure [19]. The main peaks in the FT-IR spectrum of the potassium salt are at 1076, 1040, 1003, 926, 903, 824, 775, 529, and 452 cm^{-1}. This is in agreement with the spectrum obtained from the literature [19]. Elemental analyses (EA) for $K_{17}[Eu(P_2Mo_{17}O_{61})_2]\cdot 25H_2O$ (found/calculated, wt%): Mo(48.77/49.39), Eu(10.23/10.06), and P(1.80/1.88). G4-PAMAM and poly(diallyldimethylammonium chloride) (PDDA) were purchased from Aldrich Chemical.

2.2. Films preparation

The $Eu(P_2Mo_{17})_2$/PAMAM multilayer films were fabricated as follows: the quartz slide was cleaned by immersion in the "piranha solution" containing three parts H_2O_2 (30% aqueous solution) and seven parts oil of vitriol (H_2SO_4) at 80 °C for 40 min and rinsed with copious deionized water. Then, the substrate was immersed in a solution of NH_4OH (29% aqueous solution), H_2O_2 (30% aqueous solution) and pure water with a volume ratio 1:1:5 at 70 °C for 30 min, followed by extensively washing with water. The cleaned substrate was soaked for 30 min in an aqueous solution containing 1.0 wt% PDDA, to adsorb a precursor PDDA layer that can be positively charged with an acidic solution. The treated quartz slide was alternately immersed for 30 min in 10 mM $Eu(P_2Mo_{17})_2$–0.1 M HCl and 1.0 wt% PAMAM–0.1 M HCl. After each step, the slide was rinsed with water and dried with N_2.

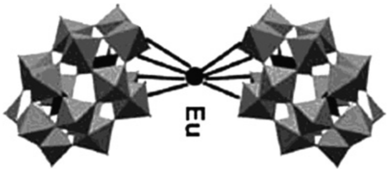

Fig. 1. Molecular structure of $K_{17}[Eu(P_2Mo_{17}O_{61})_2]$.

2.3. Measurement

FT-IR spectra were obtained on a Nicolet AVATAR 360 FTIR spectrometer (KBr pellets, 4000–400 cm^{-1}). EA was carried out by Thermo 6300 inductively coupled plasma-atomic (ICP) emission spectrometry. UV–visible measurements were conducted with a Varian Cary 500 UV–vis spectrometer. XPS was determined

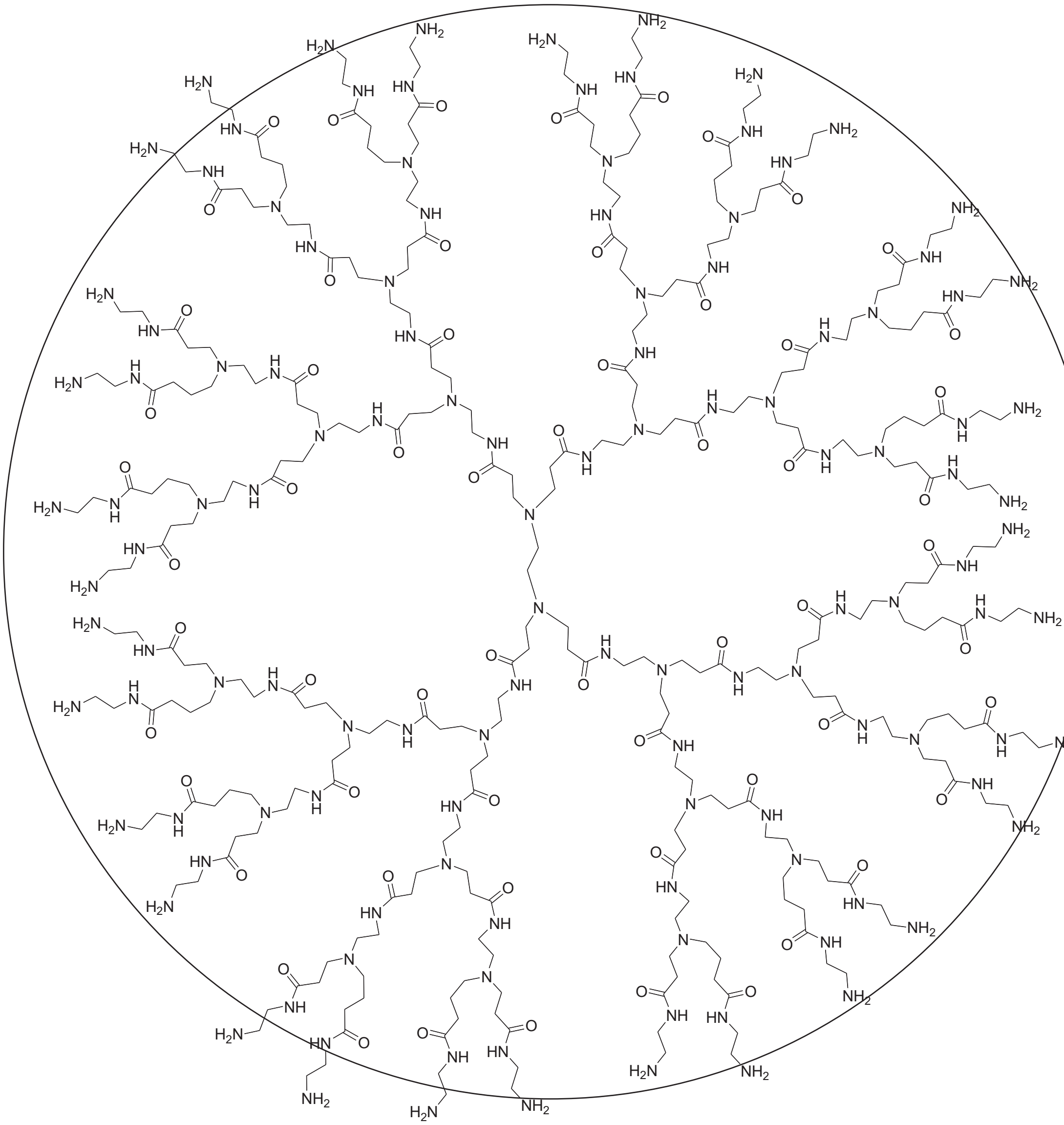

Fig. 2. Molecular structure of G4-PAMAM.