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# A color-tunable luminescent material with functionalized graphitic carbon nitride as multifunctional supports

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ABSTRACT

A color-tunable luminescent material was prepared based on the composition of functionalized graphitic carbon nitride (g-$C_3N_4$) and europium (III). The functionalized g-$C_3N_4$ layers not only behave as multifunctional supports including ligand coordinated with europium (III) and a support structure for the formation of the luminescent material, but exhibit excitation wavelength-dependent luminescence, thus the energy transfer between the functionalized g-$C_3N_4$ and europium (III) can match very well by controlling the emission wavelength of functionalized g-$C_3N_4$. The as-prepared materials was comprehensively characterized via X-ray photoelectron spectroscopy, Fourier Transform Infrared spectroscopy, X-ray scattering techniques, Ultraviolet and Visible spectrophotometer, fluorescence spectrophotometer, thermogravimetric analysis, etc. The luminescent material exhibits multi-color emissions which are consistent with the characteristic emissions of europium (III) and functionalized g-$C_3N_4$, and the photoluminescence quality and density of the europium (III) can be greatly enhanced. The brilliant optical properties of the materials make them suiting for multipurpose applications in practical fields.



## 1. Introduction

Rare earth metals constitute a series of inner transition elements and the shielding of the 4f electrons is responsible for their unique and diverse properties including high photostability, absence of blinking, extremely narrow and intense emission bands [1], large Stokes shifts and wide range of lifetimes. Thus the rare earth metals are usually employed as functional centers to coordinate with the organic molecule ligands with carboxyl groups [2–4] and amino groups etc. for constructing specific functional materials in phosphors, sensors, laser, etc [5–8]. These ligands with active sites for the coordination have obvious absorption in ultraviolet or visible region [9,10]. Due to the energy transfer between the organic ligands and the metal center [11], the absorption coefficients of rare earth complexes have been improved significantly. The energy transfer between the excited state of the ligands and the rare earth metals is called “antenna effect” [12].

As an important part of the rare earth metals, europium (III) and samarium (III) have been introduced into the functional materials to endow new and interesting composite properties by many scholars. Fan and co-workers [13] presented a simple and effective method to prapared luminescent GO by covalently functionalizing them with [Sm(TTA)$_3$(Phen)]. The weak luminescence has been greatly enhanced. For instance, composite fibers of poly (vinly pyrrolidone) and europium complex Eu(BA)$_3$(TPPO)$_2$ with strong luminescence were prepared by electrospinning [14]. These novel luminescent composite fibers have potential applications in nanodevices. Kris Driesen [15] and co-workers obtained a processable lanthanide-based luminescent molecular material by doping europium (III) complexes into a composite material consisting of PMMA and ionic liquids. The typical applications of such polymer films are in organic light emitting diodes or active optical polymer fibers for data transmission. As for europium (III) complexes, when they are excited by the light wavelengths ranging from 250 to 400 nm (maximum excitation peak at around 395 nm) [16], the characteristic emissions (579, 593, 613 and 652 nm) [17,18] of europium (III) would appear. However, it only exhibits the characteristic emissions of the europium (III).

G-$C_3N_4$ With different structures possess [19] and incorporating of nitrogen atoms in the carbon nanostructure, intrigue diverse properties including high hardness, low friction coefficient, and reliable chemical inertness [20]. Thus it can be a great potentially useful substitutes for amorphous and graphitic carbon in variety of material science applications. It ranges from catalysis [21–25] to gas and energy storage [26], and to the solar photoreduction of $CO_2$ to C1 compounds [27]. It exhibits excitation wavelength-dependent luminescence between 380 nm and 420 nm and the explanations about the mechanism have been reported [28,29]. Considering the tunable emission wavelength of the g-$C_3N_4$, the

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luminescent material was prepared and characterized using the g-$C_3N_4$ as ligand and support. When excited by single wavelength the as prepared luminescent material exhibits the bright blue and red color emissions. They are respectively corresponding to the functionalized g-$C_3N_4$ and the characteristic emissions of europium (III). Meantime, the energy transfer between functionalized g-$C_3N_4$ and europium (III) improved the light absorbance and luminescent effiency of the europium (III). The surface morphologies, microstructure and physical properties have been fully characterized via many experimental measurement methods.

## 2. Experimental section

### 2.1. Chemicals and reagents

Melamine (99%), 1, 10-phenanthroline (Phen), AIBN (2,2-Azobis) and Europium oxide ($Eu_2O_3$, 99.9%, metal basis) were purchased from Aladdin (China). Polyacrylic acid (PAA, 98%) and AA (acrylic acid) were purchased from Chengdu AiKe chemical technology co., Ltd. (China). 2-Thenoyltrifluoroacetone (TTA, 98%) was purchased from Xiya Reagent (China). All of the other chemicals used were analytical-grade reagents without further purification.

### 2.2. Synthetic procedures

The synthesis and basic composition of the whole system were shown in Scheme 1.

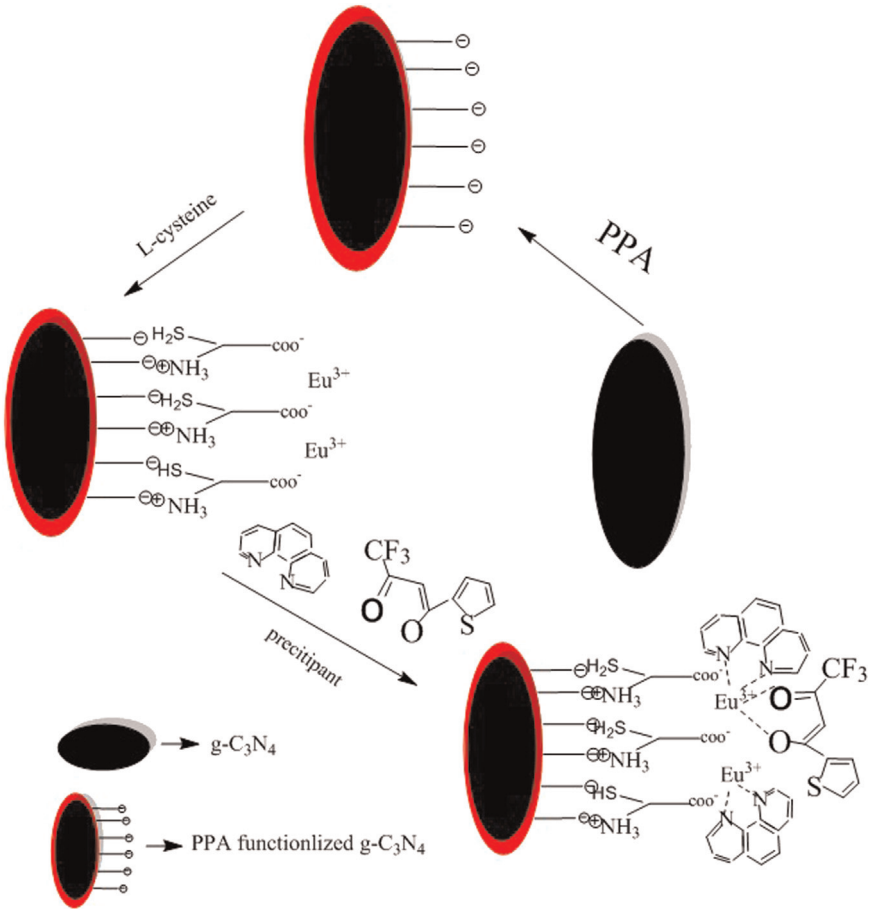
#### 2.2.1. Synthesis of functionalized G-$C_3N_4$

The preparation strategy of functionalized g-$C_3N_4$ consists of two steps. Firstly, g-$C_3N_4$ was prepared based on the previous report [22]. Typically, after being grounded for 30 min in agate mortar, melamine was transferred into a alumina crucible and heated over 3 h to 500° C with a heating rate of 2.3° C $min^{-1}$, and stayed at this temperature for 4 h. Then, the resulting sample was allowed to cool to room temperature. Secondly, the functionalization of g-$C_3N_4$ with PAA was carried out in a microwave reactor. It was under a green conditions with distilled water as solvent [13]. The as-prepared solution of the g-$C_3N_4$ (10 ml, 100 mg $ml^{-1}$) mixed with PAA (100 mg) was stirred for 10 min and then exposed to irradiation in the microwave reactor, the reaction was carried out at 85° C for 10 min and cooled to room temperature. The final product was collected by centrifugation and washed thoroughly with deionized water and then dried under vacuum at 45° C for 12 h.

Furthermore, the functionalized g-$C_3N_4$ nanoparticles can be prepared with AA [30]. As-received g-$C_3N_4$ (1.0 g) was dissolved with acetone (200 ml) in an ultrasonic bath for 10 min. Subsequently, AA (10 ml) was added into the solution under nitrogen atmosphere for 30 min. After AIBN (0.5 g) being added in, the above solution was refluxed and vigorously stirred at 55° C for 8 h. Identically, the suspension was cooled, filtered, washed and dried under vacuum at 45° C for 12 h.

#### 2.2.2. Synthesis of RE complex

$Eu(NO_3)_3$ (0.5 mmol), prepared from dissolving $Eu_2O_3$ (0.25 mmol) in diluted nitric acid with thermal treatment, was dissolved in ethanol (20 ml) to obtain $Eu(NO_3)_3$ ethanol solution.




**Scheme 1.** Schematic illustration of the synthesis and basic composition of the luminescent material.