Optical Materials 52 (2016) 92–99

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat

Tuning the chromaticity of the emission color of the copolymers containing Eu(III), Tb(III), Be(II) ions based on colorimetric principle

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ARTICLE INFO

Article history:
Received 21 August 2015
Received in revised form 29 November 2015
Accepted 3 December 2015
Available online 21 December 2015

Keywords:
Three primary colors
Colorimetric principle
White light
Copolymerization

ABSTRACT

In this work, a method of tuning the chromaticity of the emission color of the copolymers containing Eu (III), Tb(III), Be(II) ions based on colorimetric principle was proposed. The technological route from coordination to copolymerization was employed to obtain the white light macromolecular phosphor. The three primary color monomers have been synthesized and their Commission Internationale de L'Eclairage (CIE) coordinates are respectively (0.540, 0.314), (0.231, 0.463), and (0.161, 0.054). The molar feed ratios of the three primary color monomers were calculated from the CIE coordinates based on colorimetric principle. Serial copolymers have been synthesized by free radical copolymerization of the three primary color monomers and methyl methacrylate. The quantum efficiency of the copolymers was higher than that of the complex monomers. The complexes were directly boned to the polymer chain, in which the energy transfer was reduced significantly compared to the doped-polymers. The experimental values of copolymers' CIE coordinates were located in the white light region in good agreement with theoretical values. The results indicate that the chromaticity of the emission color of the copolymers containing Eu(III), Tb(III), Be(II) ions could be tuned by theoretical calculation based on colorimetric principle.

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1. Introduction

As a potential candidate for replacing conventional incandescent and fluorescent lamps, white-light emitting diodes have attracted considerable interest in recent years owing to their long lifespan, low energy consumption, high efficiency, reliability, and environmental friendliness [1–3]. Generally speaking, white light is a mixture of several pure colors. The simplest way to achieve a light source with a white appearance is to combine blue with yellow/orange primary light sources. However, only a very low color-rendering index (CRI) is obtained this way. A red, green and blue phosphor suitable for near-ultraviolet excitation enables much higher CRI values and hence a high-quality white light source. Moreover, full color displays require pure red, green, and blue emission. To the best of our knowledge, it is difficult to obtain pure emission colors from conjugated polymers or small organic molecules, due to their broad emission spectra typically with a full width at half maximum of 100–200 nm [4,5], but organic lanthanide complexes meet this requirement because of their very narrow emission of lanthanide ions [6–8]. Of all the lanthanide ions, Eu(III) ion is the best candidate for red-emitting component [9–11] and Tb(III) ion for green-emitting [12–14]. And the blue light-emitting can be conducted by $Be(BTZ)_2$ [15].

White-light emitting small organic molecules based on Tb(III) and Eu(III) complexes have been synthesized by Kido's and Li's groups [4,5]. However, small organic lanthanide complexes undergo decomposition to some degree during film formation by vacuum deposition. To avoid the decomposition, the lanthanide complexes were dispersed into polymer matrices. But this technique has the disadvantage of the non-uniform blend and dispersion of the dopants, resulting in phase separation and ionic aggregation. More seriously, energy transfer occurred among different lanthanide ions in these co-doped materials [16,17]. Intense energy transfer from Tb^{3+} to Eu^{3+} has been discovered in various matrices [18,19], in which Tb^{3+} acts as a donor and Eu^{3+} as an acceptor. Covalently bonded to a single polymer chain or as side groups, two or three lanthanide chromophores would help overcome the above-mentioned defects. Shunmugam et al. [20] reported a novel white emission functionalized polymer chelating blue-emitting Dy^{3+}, red-emitting Eu^{3+}, and green-emitting Tb^{3+} via

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http://dx.doi.org/10.1016/j.optmat.2015.12.003
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the technological means from polymerization to coordination. Yang et al. [21] reported a novel ternary copolymer containing both Tb(III) and Eu(III) complexes for white-light electroluminescence synthesized by the technological means from coordination to polymerization. The distance between different chromophores is controllable within the polymer chain. But few literatures reported that the chromaticity of the emission color of the copolymers was regulated through theoretical calculation. What's more, the three primary colors demonstrate triangle in CIE chromaticity coordinate, the tune of the three primary color needs heaps of times experiments using conditional trial-and-error method. Tuning the chromaticity of the emission color based on colorimetric principle of will gain time and cost.

Therefore, we develop a new method based on colorimetric principle to determine the feed ratios of three-primary-color complexes for white-emitting copolymers containing Eu(III), Tb(III), and Be(II) ions.

2. Experimental

2.1. Materials

Methyl methacrylate (MMA) and methylacrylic acid (MAA) were distilled and stored in a refrigerator. $EuCl_3$, $TbCl_3$, and $BeSO_4{\cdot}4H_2O$ with high purity (>99%) were obtained from Diyang Co., Shanghai. Beryllium sulfate tetrahydrate(99.98%), thenoyltrifluoroacetone (TTA, 99.99%), *o*-aminobenzoic acid (*o*-ABAH, 99.99%), undecylenic acid(UAH, 99.99%), benzothiazole (BTZ, 99.99%), and azobisisobutyronitrile (AIBN, 99.99%) were from Alfa Aesar and used as analytical reagents. All organic solvents (analytical grade) were obtained from Shanghai Chemical Reagent Company and used as received without further purification.

2.2. Synthesis of monomer $Eu(TTA)_3(UA)$

An aliquot 25 mL of ethanol solution containing 1 mmol of $EuCl_3$, 3 mmol of TTA and 1 mmol of UAH was neutralized to pH = 6–7 and then precipitated by adding 1.0 mol/L sodium hydroxide ethanol solution. The solution was refluxed while being stirred at 50 °C for 5 h. The precipitate was collected, repeatedly washed with ethanol and dried to obtain the product with the yield of 72.5%. The complex was soluble in $CHCl_3$, THF, DMSO and DMF. Elemental analysis (calculated/found): C (36.55%/36.73%), H (3.71%/3.78%); the content of Eu^{3+} ion in $Eu(TTA)_3(UA)$ (calculated/found): Eu (16.76%/16.14%). IR (KBr, cm^{-1}): 2931($\nu_{as}(CH_2)_8$), 2853($\nu_s(CH_2)_8$), 1607(νC═O), 1411(δC—H), 1304($\nu_{as}CF_3$), 1245(ν_sCF_3), 461(ν Eu—O).

If the above way is kept, the complex $Tb(o\text{-}ABA)_3(UA)_2$ was synthesized with 1 mmol of $TbCl_3$, 3 mmol of *o*-ABAH and 1 mmol of UAH. Its yield was 69.5% and the elemental analysis (calculated/found): C (48.70%/48.94%), H (5.36%/5.49%); the content of Tb^{3+} ion in $Tb(o\text{-}ABA)_3(UA)_2$ (calculated/found): Tb (20.81%/20.19%). IR (KBr, cm^{-1}): 3458($\nu_{as}NH_2$), 3359(ν_sNH_2), 2930($\nu_{as}(CH_2)_8$), 2853 ($\nu_s(CH_2)_8$), 1579(ν_{as}C═O), 1393(ν_sC═O), 531(νTb—O).

Also, the complex Be(BTZ)(MAA) was synthesized with 1 mmol of $BeSO_4{\cdot}4H_2O$, 1 mmol of BTZ and 1 mmol of MAA. Its yield was 72.4% and the synthesized complex was soluble in $CHCl_3$, THF, DMSO and DMF. Elemental analysis (calculated/found): C (63.75%/63.83%), H 4.06%/4.11%); the content of Be^{2+} ion in Be(BTZ)(MAA) (calculated/found): Be(2.81%/2.64%). IR (KBr, cm^{-1}): 2950($\nu_{as}CH_3$), 2842(ν_sCH_3), 1647(νC═C), 1608(νC—N), 668(νBe—O).

2.3. Preparation of copolymers MMA-co-$Eu(TTA)_3(UA)$-co-$Tb(o\text{-}ABA)_3(UA)_2$-co-Be(BTZ)(MAA) (PMEuTbBe)

The copolymers were synthesized by free radical copolymerization of MMA, $Eu(TTA)_3(UA)$, $Tb(o\text{-}ABA)_3(UA)_2$, and Be(BTZ)(MAA). The total concentration of the monomers was kept constant at 1.5 mol/L, the complex monomers accounted for 3.56 wt% of the total monomers, and AIBN (initiator) was 0.3 wt% of all the monomers. All the monomers and initiator were dissolved in 10 mL of dry DMSO. The solution was bubbled by purified nitrogen for 30 min to remove oxygen at room temperature, then sealed and heated at 70 °C for 48 h. After the copolymerization finished, the vicious solution was precipitated in 50 mL of methanol. The crude copolymer was further purified by several reprecipitations from DMSO to methanol and dried under vacuum at 60 °C for 6 h to obtain white solid powder with a yield of 69.4%. M_n = 138,491, M_w = 232,302, polydispersity = 1.67. T_g = 128.20 °C. ^{13}C NMR ($CDCl_3$, ppm): 17, 19, 30, 45, 52, 53, 55(aliphatic-C); 128(Ar-C); 178(COO). IR (KBr, cm^{-1}): 2952($\nu_{as}CH_3$), 2842(ν_sCH_3), 1730 (νC═O), 1270, 1244 (ν_{as}(C(O)—O)); 1194, 1150 (ν_s(C(O)—O)). The polymer is easily soluble in $CHCl_3$, THF, and DMF. The reaction formula of the copolymer can be depicted as Scheme 1.

2.4. Measurements

Elemental analysis of carbon and hydrogen was conducted on Perkin-Elemer elemental analyzer. The content of metal ion in the complexes was determined by titration with EDTA using xylenol orange as the indicator. Molecular weights were determined by GPC using a Waters Model 510 Liquid Chromatograph versus polystyrene standard using THF as eluting solvent. ^{13}C NMR spectra were measured by an Advance DMX500, 500 MHz spectrometer in $CDCl_3$. DSC measurement was carried out at a heating rate of 10 °C/min under nitrogen on Sapphire Differential Scanning Calorimeter (PerkinElmer). Fluorescence spectra were recorded with a Hitachi F-4500 fluorescence spectrometer equipped with a 450 W Xenon lamp as the excitation source. X-ray diffraction measurements were performed on a ristalloflex XRD-5000 X-ray diffractometer.

3. Results and discussion

3.1. Luminescent properties of $Eu(TTA)_3(UA)$, $Tb(o\text{-}ABA)_3(UA)_2$, and Be(BTZ)(MAA)

The excitation spectrum of $Eu(TTA)_3(UA)$ obtained by monitoring the emission of Eu(III) ion at 613 nm, as shown in Fig. 1(a), has a broad absorption band from 290 nm to 450 nm with a maximum at 378 nm, which can be assigned to the π–π∗ transition of the TTA ligand and also indicate that the complex can be excited by 365 nm of ultraviolet chip. Under being excited at 365 nm, the emission spectrum of the complex exhibits the characteristic emission bands of Eu(III) ion at 578, 590, 613, and 650 nm, corresponding to the $^5D_0$–$^7F_0$, $^5D_0$–$^7F_1$, $^5D_0$–$^7F_2$, and $^5D_0$–$^7F_3$ transitions, respectively. The transition of $^5D_0$–$^7F_2$ is an electric dipolar transition sensitive to surrounding environment, while the $^5D_0$–$^7F_1$ transition as a magnetic dipolar transition is insensitive to surrounding environment. The high intensity ratio of $^5D_0$–$^7F_2$ to $^5D_0$–$^7F_1$ indicates that the chemical environment around Eu(III) ion does not have an inversion center [22]. Therefore, the complex $Eu(TTA)_3(UA)$ displays pure red emission of Eu(III) ion.

As we can see from Fig. 1(b), there are two wide absorption bands (262–332 nm centered at 300 nm and 332–386 nm centered at 360 nm) in the excitation spectrum of $Tb(o\text{-}ABA)_3(UA)_2$ taken by monitoring the emission wavelength of Tb(III) ion at 543 nm. The peak at 300 nm is due to the π–π^* transition of the aromatic ring from the ligand. The peak at 360 nm is attributed to the intramolecular charge transfer (ICT) in *o*-ABAH. The results imply that the complex $Tb(o\text{-}ABA)_3(UA)_2$ can be also excited by the 365 nm of ultraviolet chip. The emission spectrum of

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