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Preparation and photoluminescence properties of electrospun nanofibers containing PMO-PPV and Eu(ODBM)$_3$phen

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Abstract

This communication explores a facile approach for fabricating nanofibers containing luminescent conjugated polymer, poly(2-methoxy-5-octoxy)-1,4-phenylene vinylene)-alt-1,4-(phenylene vinylene) (PMO-PPV), and rare earth complex, Eu(ODBM)$_3$phen (ODBM: 4-*n*-Octyloxydibenzoylmethanato; phen: 1,10-phenanthroline) via an electrospinning technique. The morphology and photoluminescent properties of the electrospun fibers were characterized by scanning electron microscopy, fluorescence spectrophotometer and UV optical microscopy. The electrospun fibers with diameters ranging from 70 nm to 200 nm as well as parallel orientation show strong green and red photoluminescence. This is the first but important approach towards novel applications of luminescent conjugated polymers and rare earth complex nanofibers. This kind of eletrospun nanofiber is a promising candidate for optical and electrical nanomaterials.

Keywords: Nanofibers; Electrospinning; Conjugated polymers; Rare earth complex; Photoluminescence

1. Introduction

Exploring novel methods for fabricating one-dimensional nanostructural materials have gained considerable attention in recent time owing to their potential applications. Electrospinning has been found to be a unique and cost-effective approach for fabricating high long-aspect ratio ultrafine fibers with diameters ranging from several microns down to about 10 nm [1]. Various multi-functional nanofibers were prepared via electrospinning technique in recent years [2,3]. Nanofibers with photoluminescence properties can provide us a wide range of applications in nanophotovoltaic devices, photodiodes, sensors, wave-guiding and all-optical switching [4].

The optoelectronic properties of conjugated polymers and metal complexes are highly interesting objects for a broad range of applications in light-emitting diodes (LEDs), light-emitting electrochemical cells (LECs) and high-density optical storage. Poly(*p*-phenylene vinylene) (PPV) and its derivatives are of remarkable importance for conjugated polymer with photoluminescence and electroluminescence properties due to their high efficiency and good environmental stability [5]. Europium (III) complexes show a strong red fluorescence by a UV light excitation due to the antenna effect of ligands and *f*–*f* electron transition of Eu^{3+}[6]. Madhugiri and co-workers [7] obtained leaf-like fibers by electrospinning a PPV derivative, poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylenevinylene) (MEH-PPV). Unluckily, most conjugated polymers and metal complexes are not suitable for electrospinning due to low molecular weight and low viscosity of solution.

In this study, we present a facile approach for fabricating two nanofibers with strong photoluminescence properties by electrospinning the blend solutions of PMO-PPV/PMMA or Eu(ODBM)$_3$phen/PMMA. The chemical structures of PMO-PPV and Eu(ODBM)$_3$phen were shown in Fig. 1. Introducing the long alkyloxy in ligand ODBM can improve the luminescence properties of complex material and increase the compatibility between the complexes and PMMA. Poly(methyl methacrylate) is a transparent amorphous polymer with

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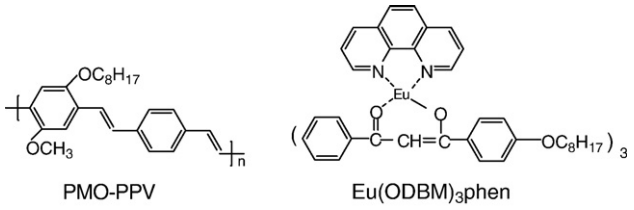

Fig. 1. Chemical structures of PMO-PPV and Eu(ODBM)$_3$phen.

particular optical properties and can thus be a suitable light-transparent material.

2. Experimental

PMO-PPV was synthesized according to the procedure as described in the reference [8] and its average molecular weight is in the range of 7000–10,000 (M_w). Eu(ODBM)$_3$phen was prepared according to the reference [9] in our lab. Poly(methyl methacrylate) (PMMA, $M_w = 8.7 \times 10^4$) was commercial product (Roehm Gmbh Chemistry Factory, Germany).

Electrospun nanofibers were prepared by adding 0.2 g PMO-PPV (or 0.2 g Eu(ODBM)$_3$phen) and 1 g PMMA in 10 mL mixed solvent composed of chloroform and tetrahydrofuran and *N*,*N*-dimethylformamide (2:1:1). Lithium chloride (LiCl, Aldrich) of 0.1 g was used as an additive in order to increase the conductivity of the solution. The solution was stirred for 1 h at room temperature. The mixture solution was placed into a syringe and was pumped continuously through the die via a syringe pump. A potential of 40 kV was applied to the die, the distance between the die and counter electrodes amounting to 15–20 cm. The fibers were finally deposited on an aluminum foil or a quartz flake located on top of the counter electrode.

The morphology of electrospun fibers was characterized by scanning electron microscopy (SEM) using a Hitachi S-4100 at 10 kV accelerating voltage. Fluorescence spectra of the samples were recorded with a Perkin-Elmer LS55 fluorescence spectrophotometer. The fluorescent optical microscopic image was observed with a Leica DMRX microscopy equipped with a Leica DC 200 digital camera and a UV lamp emitting in the 340 nm–380 nm wavelength range.

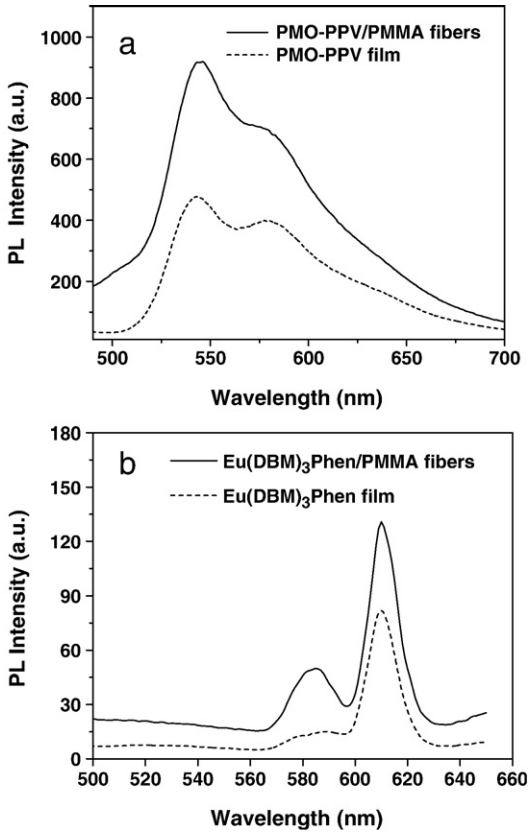

Fig. 3. PL spectra of (a) 20 wt.% PMO-PPV/PMMA eletrospun fibers and net PMO-PPV films, and (b) 20 wt.% Eu(ODBM)$_3$phen/PMMA eletrospun fibers and net Eu(ODBM)$_3$phen films.

3. Results and discussion

Nanofibers containing conjugated polymer or rare earth complex can be achieved by electrospinning the solutions of PMO-PPV/PMMA or Eu(ODBM)$_3$phen/PMMA. PMO-PPV (or Eu(ODBM)$_3$phen) and

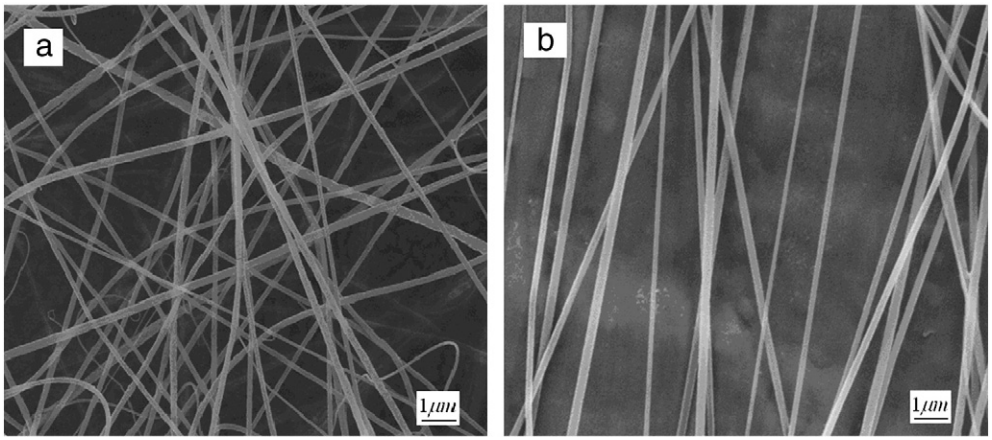

Fig. 2. SEM images of (a) 20 wt.% PMO-PPV/PMMA eletrospun fibers and (b) 20 wt.% Eu(ODBM)$_3$phen /PMMA parallel orientation of the eletrospun fibers.

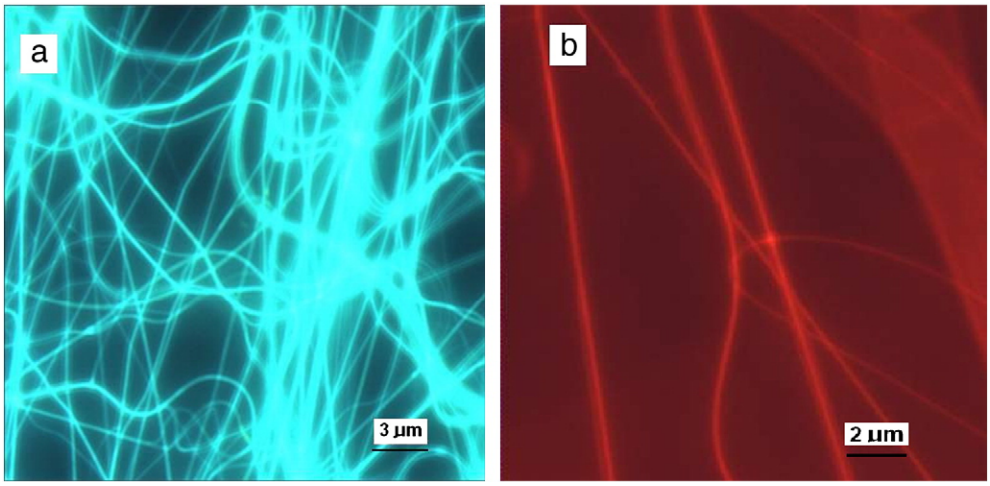

Fig. 4. Fluorescent optical microscope images of (a) 20 wt.% PMO-PPV/PMMA and (b) 20 wt.% Eu(ODBM)$_3$phen /PMMA eletrospun fibers on a quartz flake.

PMMA were dissolved in mixed solvent composed of chloroform and tetrahydrofuran and *N*,*N*-dimethylformamide (2:1:1). The mixture solution was placed into a syringe and was pumped continuously through the die via a syringe pump. The fibers were deposited on an aluminum foil or a quartz flake located on top of the counter electrode. While electrospinning PMMA/$CHCl_3$ solution, a lot of beads exist on electrospun PMMA fibers due to poor conductivity of PMMA/$CHCl_3$ solution, which can be suppressed by addition of 1% LiCl in a mixed solution composed of chloroform and tetrahydrofuran and *N*,*N*-dimethylformamide (2:1:1) with PMMA. As shown in Fig. 2(a), the nanofibers with smooth and less beads were obtained by electrospinning a 10 wt.% PMMA solution containing 2 wt.% PMO-PPV in mixing solvent of $CHCl_3$/THF/DMF (2:1:1). A parallel orientation of the nanofibers containing Eu(ODBM)$_3$phen was shown in Fig. 2(b), which was achieved by the method reported previously [10]. A cylindrical collector rotating at a speed of up to 3500 rpm was used in the case.

The photoluminescence (PL) spectra of the eletrospun nanofibers were presented in Fig. 3. As compared to the PL spectra of the net PMO-PPV film, 20 wt.% PMO-PPV/PMMA eletrospun fibers showed a same emission peaks at the range of 500–600 nm in Fig. 3(a). Both the fibers and the film show an emission λ_{max} of 549 nm when they were excited with a 466 nm excitation light, the emission maximum was red shifted compared to 517 nm of PMO-PPV solution. Similar red shifts in emission for solid state sample of PPV derivatives when compared to solutions were due to the increase in the HOMO-LUMO energy gap caused by conformational distortions in solution [7]. 20 wt.% Eu(ODBM)$_3$phen/PMMA eletrospun fibers show a narrow emission peak at 610 nm (Fig. 3b), the same as that of net Eu(ODBM)$_3$phen film and a slight blue shifted compared to 615 nm of Eu(ODBM)$_3$phen/$CHCl_3$ solution. The PL intensity of 20 wt.% PMO-PPV/PMMA eletrospun fibers (Fig. 3a solid line) or 20 wt.% Eu(ODBM)$_3$phen/PMMA eletrospun fibers (Fig. 3b solid line) are much stronger than that of net PMO-PPV film (Fig. 3a dashed line) or net Eu(ODBM)$_3$phen film (Fig. 3b dashed line), respectively. In order to illuminate the effect of the concentration of PMO-PPV and Eu(ODBM)$_3$phen on PL intensity, we measured the PL spectra of PMO-PPV/PMMA and Eu(ODBM)$_3$phen/PMMA solutions containing 20–80 wt.% PMO-PPV or Eu(ODBM)$_3$phen. The results indicate the PL intensity decreases linearly with the concentration of PMO-PPV or Eu(ODBM)$_3$phen increasing. This implies that PMMA can improve the photoluminescence properties of PMO-PPV/PMMA or Eu(ODBM)$_3$phen/PMMA blending solution due to decreased concentration quenching. 20 wt.% PMO-PPV/PMMA nanofibers (Fig. 4a) show a very strong green-yellow luminescence excited with a UV lamp of 380 nm by a fluorescence optical microscopy. Similarly, a red luminescence originated from Eu(III) complex can be observed clearly from 20 wt.% Eu(ODBM)$_3$phen/PMMA nanofibers (Fig. 4b).

4. Conclusions

The luminescent nanofibers were obtained by electrospinning the solution of PMO-PPV, Eu(ODBM)$_3$phen and PMMA. The electrospun fibers with diameters ranging from 70 nm to 200 nm as well as parallel orientation show strong green and red photoluminescence properties. This kind of eletrospun nanofiber is a promising candidate for optical and electrical nanomaterials.

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