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Preparation and luminescent properties of one-dimensional $[Ru(Bphen)_2dppz]Cl_2$/PVP composite fibers by electrospinning

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Abstract

One-dimensional nanomaterials, PVP (poly(vinylpyrrolidone)) fibers doped with $[Ru(Bphen)_2dppz]Cl_2$ (Bphen = 4,7-diphenyl-1,10-phenanthroline; dppz = dipyrido[3,2-*a*:2′,3′-*c*]phenazine) were prepared by electrospinning technique. The luminescent properties of the composite fibers with diameters between 500 and 900 nm were investigated. Bright red emission centering at 596 nm attributed to the metal (dπ) to ligand (π^*) charge-transfer (^{3}MLCT) transition was observed. The composite fibers doped 0.20 wt.% ruthenium(II) complex were optimal, which exhibited the maximum luminescent intensity.

Keywords: Electrospinning; Fibers; Ruthenium(II) complex; Luminescence

1. Introduction

In recent years, electrospinning technique has attracted increasing attention because it is a simple and low-cost method for producing continuous ultrafine polymer fibers with diameters ranging from tens of nanometers to several micrometers [1–4]. These fibers with high specific surface area and porous structure lead themselves to a wide range of applications including filtration devices, membranes, optics, protective clothing, molecular templates and sensors [5–10]. So far, many electrospun polymer nanofibers with electrical or photoelectronic properties have been reported, and their potential applications have been demonstrated in the fabrication of nanoscale electrical or photoelectronic devices [11,12].

Ruthenium(II) complexes are among the most widely studied organometallic molecules due to their variety of attractive functions based on luminescent properties with a long excited state lifetime, redox properties, and relatively high chemical and thermal stability [13]. Such unique features make the ruthenium(II) complexes doped materials quite attractive as optical sensors [14], photocatalysts [15], photoelectrodes for solar cells [16]. To the best of our knowledge, there is no literature on the preparation of one-dimensional nanofibers doped with ruthenium(II) complexes by electrospinning. It is expected that electrospinning will develop as a new technique to prepare nano- or microscale ruthenium(II) complexes-doped composite fibers. Among the ruthenium(II) complexes, the Ru(II) complex using dppz as ligand possesses long excited state lifetime, high quantum yield, large Stokes' shifts and relatively high chemical and thermal stability compared to others [17]. Herein, we first report the preparation and luminescent properties of $[Ru(Bphen)_2dppz]Cl_2$/PVP composite fibers using electrospinning method.

2. Experimental

2.1. Materials

$[Ru(Bphen)_2dppz]Cl_2$ was synthesized according to the modified procedures [17]. The chemical structure is depicted in Scheme 1. Poly(vinylpyrrolidone) (PVP, $M_w = 60{,}000$) was supplied by Beijing Yi Li Chemical Factory. All reagents were analytical grade.

2.2. Preparation of spinning solutions

PVP was dissolved in ethanol/dichloromethane mixed solvents with the weight ratio of 50/50 to prepare a 25 wt.% solution. A controlled amount of

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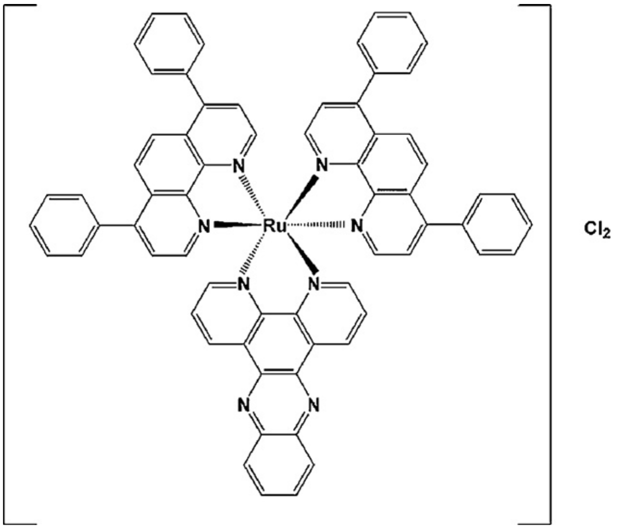

Scheme 1. Chemical structure of $[Ru(Bphen)_2dppz]Cl_2$.

ruthenium(II) complex (0.10, 0.15, 0.20, 0.30 wt.%) was dissolved in 25 wt.% PVP solutions under magnetic stirring for 24 h at room temperature.

2.3. Electrospinning process

The electrospinning apparatus were similar to those described before [4]. For electrospinning, each mixed solution was placed in a 5 ml glass syringe, the opening end of which was connected to a plastic needle (the inner diameter = 0.6 mm) being used as the nozzle. The anode terminal of a high-voltage generator was attached to a copper wire inserted into the polymer solution in the glass syringe. A piece of aluminum foil was used as the collector plate and it was connected to the grounding electrode. The sample of Fig. 6 was prepared by electrospinning the mixed solution doped with 0.20 wt.% ruthenium(II) complex. The glass slide was used as the collecting substrate and the collection time is 3 s. The applied voltage was 18 kV, and the collection distance was 25 cm. The electrospinning was carried out in air.

2.4. Characterization of fibers

UV–vis and fluorescence spectra were recorded on a Shimadzu UV-3150 spectrophotometer and a Hitachi F-4500 spectrophotometer, respectively. The morphologies of the composite fibers were observed with a Hitachi S-4800 scanning electron microscopy and a Nikon TE2000-U fluorescence microscopy using the mercury lamp as the power supply. The fluorescence lifetimes of ruthenium(II) complex in fibers and glassy solution were obtained with a 266 nm light generated from the Fourth-Harmonic-Generator pump, which used the pulsed Nd:YAG laser as the excitation source.

3. Results and discussion

Fig. 1 shows a series of SEM images of the composite fibers from electrospinning mixed solutions with the ruthenium(II) complex concentration from 0.10 to 0.30 wt.%. It is obvious that the morphology of the fibers is smooth, uniform and without branch structures. The corresponding average diameter and the diameter distribution of the composite fibers are presented in Fig. 2. The smallest average diameter of the composite fibers is obtained at the concentration of 0.15 wt.% (637 nm), and the largest one is obtained at the concentration of 0.20 wt.% (747 nm). At the concentration of 0.10 wt.% and 0.30 wt.%, the average diameters of fibers are 697 nm and 737 nm, respectively.

Fig. 3 shows the absorption spectrum of ruthenium(II) complex in ethanol solution and the inset show the solid diffuse reflection UV–vis spectra of 0.20 wt.% ruthenium(II) complex-doped composite fibers (a) and pure ruthenium(II) complex (b).

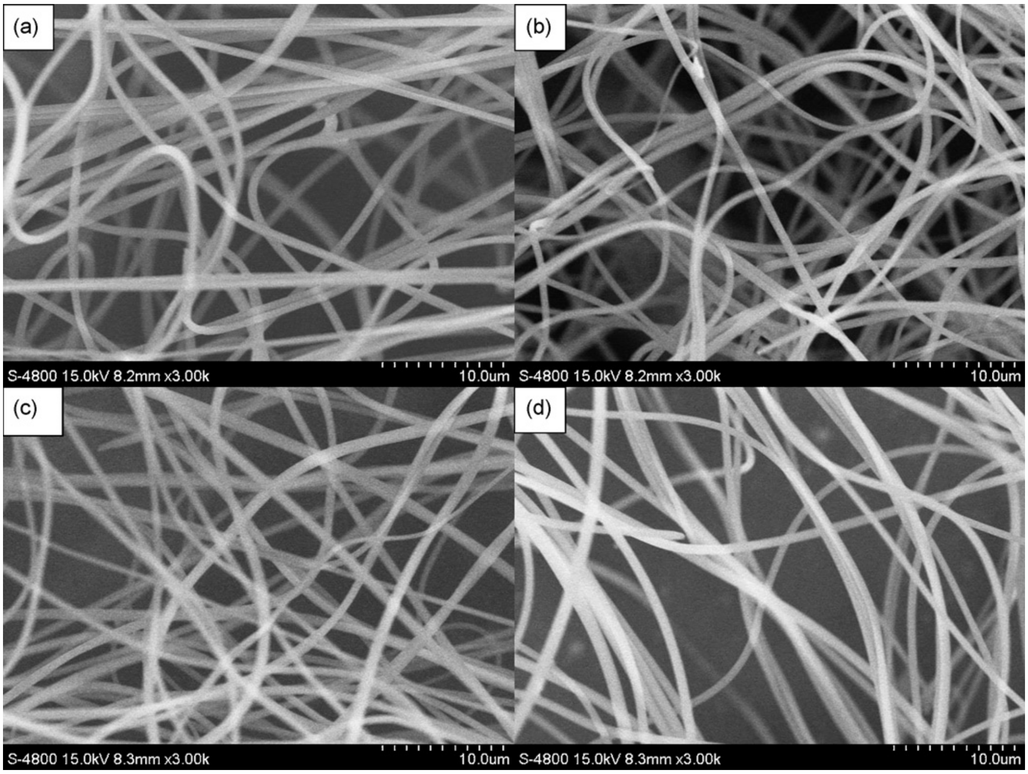

Fig. 1. The SEM images of the composite fibers with different ruthenium(II) complex concentration, (a) 0.10 wt.%, (b) 0.15 wt.%, (c) 0.20 wt.%, (d) 0.30 wt.%.

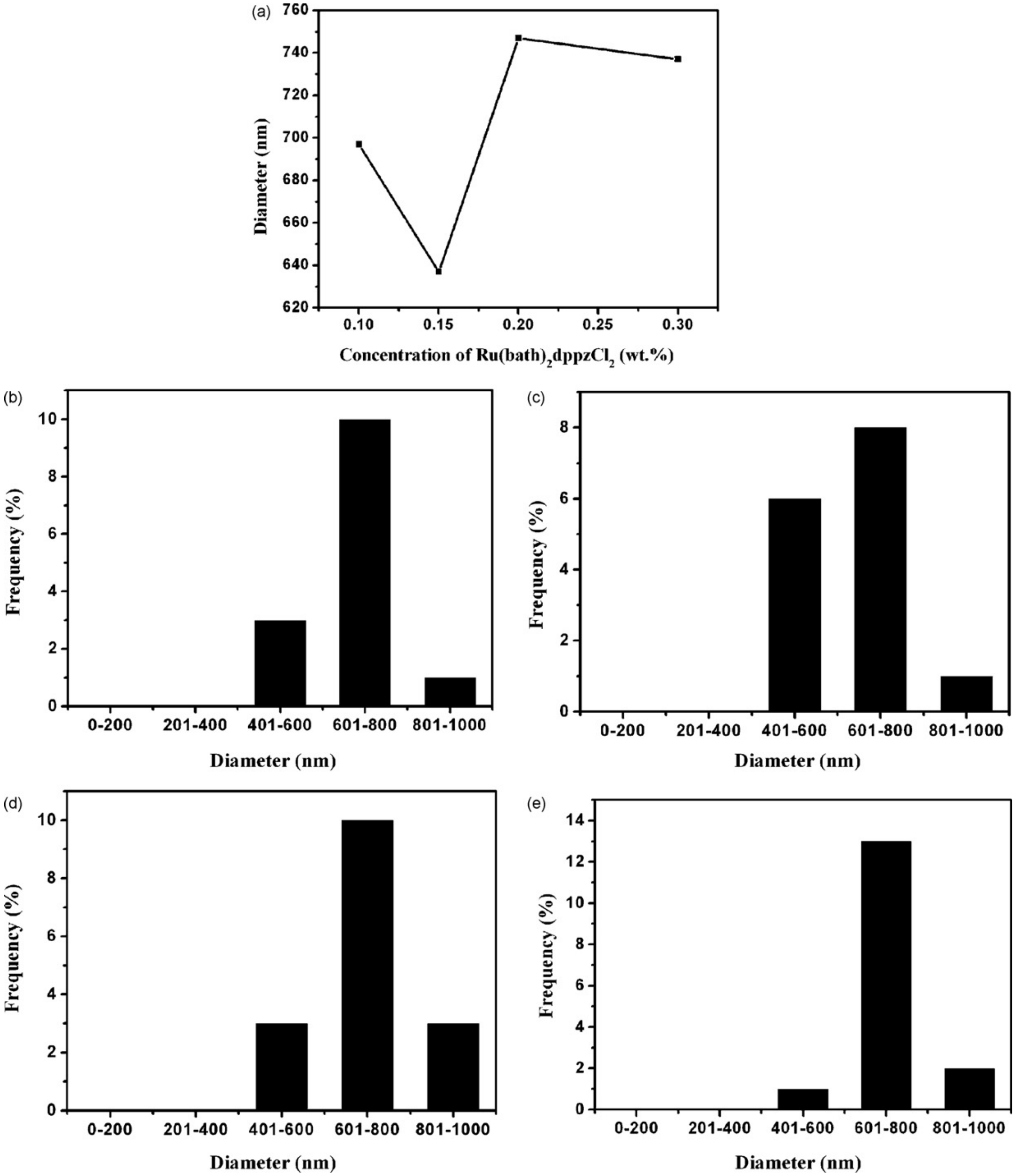

Fig. 2. Average diameter (a) and diameter distribution of the composite fibers with different concentration of ruthenium(II) complex: (b) 0.10 wt.%, (c) 0.15 wt.%, (d) 0.20 wt.%, (e) 0.30 wt.%.

The absorption peaks at around 275 and 370 nm are ascribed to ligands centered ($\pi \rightarrow \pi^*$) transitions, and the broad absorption band centered at around 450 nm is assigned to metal-to-ligand charge-transfer (MLCT) ($t_{2g}(Ru) \rightarrow \pi^*(L)$) transition [18]. The solid diffuse reflection UV–vis spectrum of composite fibers is very similar to that of pure ruthenium(II) complex, indicating that the molecule remained intact during the process of encapsulation.

The fluorescence feature of $[Ru(Bphen)_2dppz]Cl_2$ is the typical triplet MLCT process, which is attributed to the emission from the triplet MLCT excited state (^{3}MLCT) to the ground state [19]. Fig. 4 shows the emission spectra of ruthenium(II) complex in different states. It is found that ruthenium(II) complex in glassy state exhibits vibronic structured emission with vibrational spacing ($\Delta\nu = 1130\,\mathrm{cm}^{-1}$), characteristic of stretching vibration of aromatic ring, and there is no obvious shift of the emission maxima for ruthenium(II) complex in composite fibers and in ethanol solution. In order to examine the effect of doped concentration of ruthenium(II) complex on the luminescent intensity, four different amounts, 0.10, 0.15, 0.20,

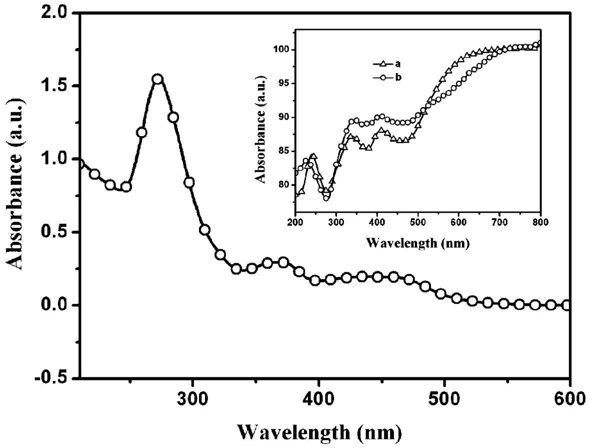

Fig. 3. UV–vis absorption spectrum of ruthenium(II) complex in C_2H_5OH with the concentration of 1×10^{-5} mol/L. The inset show the diffuse reflection spectra of 0.20 wt.% ruthenium(II) complex-doped composite fibers (a) and pure ruthenium(II) complex (b).

0.30 wt.% of ruthenium(II) complex, were doped to the fibers. The corresponding emissive spectra are presented in Fig. 5. It is obvious that the luminescent intensity increases with the increment of doping concentration, and reaches the maximum at the doping concentration of 0.20 wt.%. At 0.30 wt.%, the luminescent intensity decreases, which indicates concentration quenching may dominate when the concentration is higher than 0.20 wt.%. In other words, when the concentration is higher than 0.20 wt.%, the strong self-quenching and triplet–triplet annihilation between ruthenium(II) complex in the composite fibers may decrease the emission efficiency. The fluorescence photography (Fig. 6) of ruthenium(II) complex-doped composite fibers at the concentration of 0.20 wt.% shows that they emit bright red light and the luminosity is uniform, indicating this kind of composite fibers may be used as red-light nanodevices.

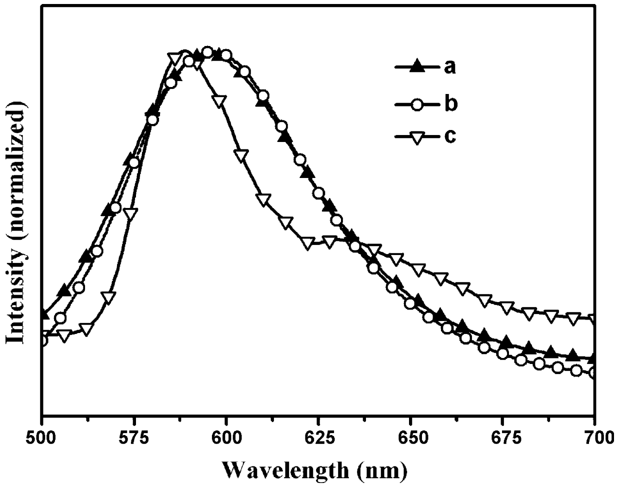

Fig. 4. Emission spectra of ruthenium(II) complex in different states. (a) 0.20 wt.% ruthenium(II) complex-doped composite fibers, (b) solution of ruthenium(II) complex in ethanol with the concentration of 1×10^{-4} mol/L, and (c) 77 K EtOH/MeOH (v/v = 4/1) glassy solution of ruthenium(II) complex with the concentration of 1×10^{-4} mol/L.

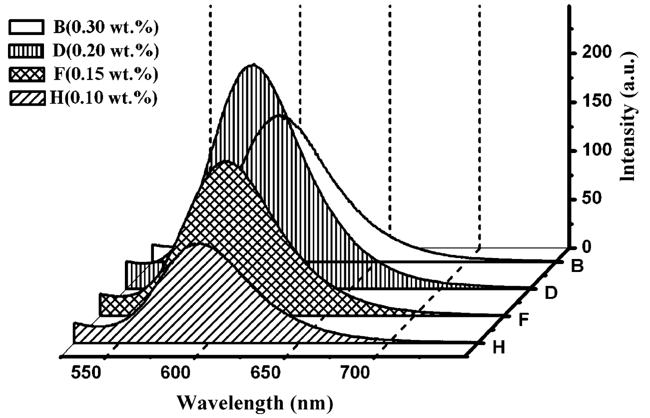

Fig. 5. Emission spectra of the composite fibers with different ruthenium(II) complex concentration. Excitation at 480 nm.

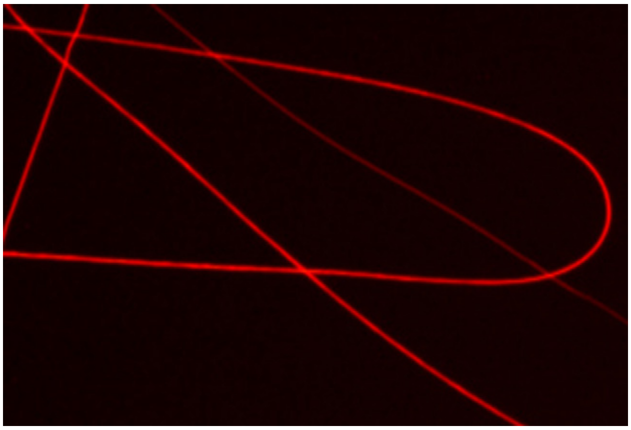

Fig. 6. The fluorescence photography of ruthenium(II) complex-doped composite fibers at the concentration of 0.20 wt.%.

The key data of the lifetime measurements are listed in Table 1. The fluorescence decay data of ruthenium(II) complex in composite fibers and glassy solution can be fit very well to a single exponential decay curve expressed by:

$$I(t) = \alpha \exp\left(\frac{-t}{\tau}\right)$$

where $I(t)$ is the fluorescence intensity at time t, τ the decay time, and α the pre-exponential factor. It indicates that the ruthenium(II) complex occupies only one site in composite fibers as well as in glassy solution and every $[Ru(Bphen)_2dppz]Cl_2$ molecule exists as a monomer in composite fibers.

Table 1
The luminescence lifetimes of ruthenium(II) complex in composite fibers and in glassy solution

States (T (K))	Emission λ_{em} (nm)	Luminescence lifetimes (μs)	R^2
In composite fibers[a] (298)	596	2.96	0.9955
In glassy solution[b] (77)	589	8.09	0.9995

[a] 0.20 wt.% ruthenium(II) complex-doped composite fibers.

[b] 10^{-4} mol/L EtOH/MeOH (4:1, v/v) solution.

4. Conclusions

A simple electrospinning method was used to prepare ruthenium(II) complex-doped composite fibers with diameters in the range of 500–900 nm. They emit bright red light with uniform intensity, and the best doping concentration of ruthenium(II) complex was 0.2 wt.%. Single exponential decay of composite fibers indicates that every $[Ru(Bphen)_2dppz]Cl_2$ molecule exists as a monomer in composite fibers. Overall, electrospinning is a novel and available technique to fabricate ruthenium(II) complex-doped composite fibers. They may find applications in nanodevices.

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