Chiral Zinc Phenylalanine Nanofibers with Fluorescence

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Chiral Zn(II)/D-,L-phenylalanine (Phe) bio-coordination polymer nanofibers with fluorescence were prepared by fast coordination-assisted assembly. The synthetic strategy is based on the fact that the Zn2+ ions were linked to oxygen atoms from carboxylate groups of the D- or L-amino acid by coordination interactions to form the chiral polymers. The Zn(II)/D-,L-Phe nanofibers had homogeneous diameters in the range of 700–900 nm and ultra-long length in several hundred micrometers, and the surface of the fiber was extremely smooth. In addition, the enantiomers of Zn(II)/Phe nanofibers exhibited both optical activity and fluorescent property in the solid state, which has great potential for application in the field of biomimetic nanofabrication and micro-/nano-optoelectronics.

Keywords: Bio-Coordination, Chirality, Fluorescence, Nanofibers.

1. INTRODUCTION

Self-assembly of one-dimensional (1-D) micro- and nanoscale structures has gathered much attentions for their promising applications in catalysis,1 optics,2 sensing,3 data storage,4 separations5 and biomedicine in recent years,6 and a variety of viable strategies are developed to prepare 1-D nanoscale inorganic materials and polymers.7 Bio-coordination polymers (BCPs),9 which consist of repeating amino acid units interconnected by metal ion nodes through coordination interactions, are considered to be promising 1-D biomaterials due to their unique and highly tailorable properties.10–12 In our work, the chiral Zn(II)/Phe BCP nanofibers were successfully prepared through a fast coordinative polymerization,13 and the synthetic strategy is based on the fact that the Zn2+ ions were linked to oxygen atoms from carboxylate groups of the D- or L-amino acid through coordination interactions as illustrated in Figure 1. In addition, the corresponding morphology, composition, crystal structure and optical property of the Zn(II)/Phe nanofibers were also investigated. To the best of our knowledge, it is the first report of the chiral BCP nanofibers exhibiting both optical activity and fluorescent property in the solid state, which has great potential for application in the field of biomimetic fabrication and micro-/nano-optoelectronics.

2. EXPERIMENTAL DETAILS

2.1. Materials

Zinc nitrate (Zn(NO3)2·6H2O), sodium hydroxide (NaOH), D-Phe, L-Phe and DL-Phe were purchased from Aladdin. These chemicals were used without further purification.

2.2. Preparation of Zn(II)/Phe Nanofibers

Add NaOH (2 mmol, 80 mg) into Phe (2 mmol, 330 mg) solution (10 mL deionized water), then stir the mixture for 0.5 h. Zn(NO3)2·6H2O (1.5 mmol, 446 mg) dissolved in deionized water (2 mL) was added drop by drop into the solution of Phe and NaOH, and the polymerization was completed immediately. The final Zn(II)/Phe BCP nanofibers were obtained from as-prepared products washed with deionized water and sedimented several times until all unreacted precursors and salts were removed.

2.3. Characterization of Zn(II)/Phe Nanofibers

The morphologies of the final Zn(II)/Phe nanofibers were characterized by scanning electron microscopy (SEM, Hitachi S-4800) under the accelerating voltage of 10 kV. The elemental analysis was accomplished by energy-dispersive X-ray spectroscopy (EDX, Horiba EMAX7593-H) and the accelerating voltage was 15 kV. FT-IR
3. RESULTS AND DISCUSSION

In our experiment, the white floccules were instantly formed when a drop of Zn(NO₃)₂·6H₂O solution was added into the aqueous solution containing D-,L-Phe and NaOH. After dripping out of all the metal salts solution, the entire aqueous phase was homogeneously filled with white floccules as shown by the optical microscopy images in Figures 2(a) and (b), and no difference in the macroscopical morphology of the chiral materials was observed. The microcosmic morphology of the Zn(II)/Phe nanofibers was examined by SEM. Low-magnification SEM images (Figs. 2(c, d)) showed that the high-density Zn(II)/D-,L-Phe nanofibers were uniformly distributed. Occasionally, a bundle of fibers were also observed. And SEM images at high magnification displayed that the single Zn(II)/D-,L-Phe nanofiber (Figs. 2(e, f)) had an extremely smooth surface and homogeneous diameters in the range of 700–900 nm, and the insets of the typical optical microscopy images revealed the nanofibers were ultra-long with the length of several hundred micrometers.

The composition of Zn(II)/D-,L-Phe nanofibers were further investigated. The EDX analysis (Figs. 3(a, b)) of the nanofibers confirmed the existence of Zn, C, and O, and the chiral pairs had the same elemental composition. The Zn peak indicated the existence of Zn(II) in the nanofibers, and the signals of C, O are from the constituent Phe units. The Si signal was attributed to the silicon wafer used as the sample substrate.

The infrared spectra of the Zn(II)/D-Phe nanofibers (Red line in Fig. 4(a)) showed that Zn atoms were coordinated to oxygen atoms from carboxylic groups of the Phe ligands, as given proof of the characteristic symmetric and asymmetric COO– stretching vibration focused on 1623 cm⁻¹ and 1408/1388 cm⁻¹, respectively. The above result might be explained that the Phe, NaOH and Zn²⁺ ions are highly soluble in deionized water, and the H⁺ ions from H₃N⁺ groups of the Phe were neutralized by OH⁻ ions from NaOH, in other words, the Phe was deprotonated. Consequently, the Zn²⁺ ions were more conveniently linked to oxygen atoms from carboxylate groups of the Phe through coordination interactions, and the NH₂...
groups were easy to obtain, which corresponded to the symmetric and asymmetric stretching vibration of N–H bonds in NH₂ groups at 3257 and 3334 cm⁻¹ in the spectra. While before the coordination interaction, the infrared spectra of the D-Phe (Black line in Fig. 4(a)) showed that a broad, strong band in the region 3330–2770 cm⁻¹ and a broad, weak band in the region 2640–2220 cm⁻¹ were attributed to the stretching vibration of the H₃N⁺ groups. From 2220 to 1961 cm⁻¹, one can confirm the antisymmetric deformation vibration and the hindered internal rotation of the H₃N⁺ groups. And the infrared spectra characteristics of Zn(II)/D-Phe nanofibers was similar to that of the Zn(II)/L-Phe nanofibers.

Next, the crystal structures of the Zn(II)/D-,L-Phe nanofibers were tested by XRD (Fig. 5). The crystalline character could be confirmed by the data, however, the determination of their single crystal structure and other relative detailed analysis on structure are not feasible due to their nano-scale diameter.¹³

Furthermore, the optical activity and fluorescent property of the Zn(II)/D-,L-Phe nanofibers were studied. As displayed in Figures 6(a) and (b), the Zn(II)/D-,L-Phe nanofibers had almost the same UV-vis absorption characteristics with two relatively narrow absorption peaks at ~223 nm and ~263 nm. The former, higher energy band may be attributed to the σ–σ⁺ transition of the C–C bonded system, while the latter, lower energy band can be assigned to the π–π⁺ transition of the benzene rings according to previous reports.¹⁴ The CD spectra of the enantiomeric Zn(II)/D-,L-Phe nanofibers in Figure 7 exhibited an opposite Cotton effect with the wavelength at 338 nm near the absorption of the Zn(II) complex.¹⁵ The shape and magnitude of these Cotton effects clearly showed the chiral coordination of the metal ion in the nanofibers, indicating their enantiospecific interactions with D- or L-Phe as the chiral template.¹⁶

Figure 8(a) presented the fluorescence emission spectra of Zn(II)/D-Phe nanofibers at excitation wavelengths of λₑₓ = 222 nm. In comparison to the spectrum of the D-Phe (emission peak at 294), the emission spectrum of the Zn(II)/D-Phe nanofibers seemed to be red-shifted to 300.5 nm. And Figure 8(b) showed the fluorescence emission spectra of Zn(II)/D-,L-Phe nanofibers, indicating their enantiospecific interactions with D- or L-Phe as the chiral template.¹⁶

Fig. 3. (a–b) EDX data of Zn(II)/D-,L-Phe nanofibers.

Fig. 4. FT-IR spectra of (a) Zn(II)/D-Phe nanofibers (red) and D-Phe (black), (b) Zn(II)/L-Phe nanofibers (red) and L-Phe (black).

Fig. 5. X-Ray Powder diffraction patterns of Zn(II)/D-Phe nanofibers (black) and Zn(II)/L-Phe nanofibers (red).

Fig. 6. UV-vis absorption spectra of Zn(II)/D-,L-Phe nanofibers (red) and D-,L-Phe (black).

Fig. 7. CD spectra of Zn(II)/D-,L-Phe nanofibers.
emission peak of Zn(II)/L-Phe nanofibers (excitation wavelengths of $\lambda_{ex} = 222$ nm) red-shifted to 308 nm compared to the 299.5 nm emission peak of the L-Phe. The red shift of the fluorescence emission spectra of Zn(II)/D-, L-Phe nanofibers relative to D-, L-Phe might be attributed to the efficient intramolecular charge transfer from oxygen atoms in carboxylic groups of the Phe ligands to Zn(II). It should be noted that the enantiomer nanofibers exhibited a little variance in the emission peaks at the almost same excitation wavelengths, which might be caused by the difference of the solid power particle sizes, thickness of the adsorbed layer, solid surface absorption of the excitation light and different angles of light signal when preparing different samples in the solid state.

Also, we mixed the Zn(II) solution with the racemes phenylalanine. The flat sheets in hundred micrometers as shown in the optical image of Figure 9 instead of nanofibers were observed after mixing.

Fig. 6. (a–b) UV-vis spectra of the Zn(II)/D-, L-Phe nanofibers.

Fig. 7. CD spectra of Zn(II)/D-Phe nanofibers (black) and Zn(II)/L-Phe nanofibers (red).

Fig. 8. Fluorescence emission spectra of (a) Zn(II)/D-Phe nanofibers (red) and D-Phe (black) and (b) Zn(II)/L-Phe nanofibers (red) and L-Phe (black) excited at 222 nm.

Fig. 9. Photomicrograph of Zn(II)/racemes Phe.
4. CONCLUSIONS

We successfully synthesized BCP Zn(II)/D-,L-Phe nanofibers through coordination-assisted assembly. The chiral nanofibers had homogeneous diameters in the range of 700–900 nm and ultra-long length in several hundred micrometers, and the surface of the fiber was extremely smooth. The enantiomers of Zn(II)/Phe nanofibers exhibited both optical activity and fluorescent property in the solid state, which has great potential for application in the field of biomimetic nanofabrication and micro-/nano-optoelectronics.

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References and Notes


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