

Eu(TTA)₃phen Nanobelts with Enhanced Luminescent Properties Prepared by Self-assembly

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Crystalline Eu(TTA)₃phen (TTA is the conjugated base of 2-thenoyltrifluoroacetone, phen represents 1,10-phenanthroline) nanobelts were first prepared by solution-phase self-assembly. It was found that the concentration of Eu(TTA)₃phen and solvent could impose obvious effect on the morphologies of the resultant products. The as-prepared crystalline Eu(TTA)₃phen nanobelts show enhanced photoluminescence (PL) intensity over that of Eu(TTA)₃phen molecules dissolved in tetrahydrofuran (THF) at the same concentration.

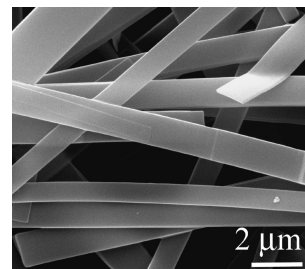


Figure 1. FE-SEM image of the as-prepared products.

In recent years, one-dimensional (1D) organic functional nanomaterials such as nanowires, nanobelts, and nanotubes have attracted much attention because of their unique chemical, physical, and mechanical properties¹ and promising applications in color-tunable display,² field-effect transistors,³ chemical sensors,⁴ optical waveguides,⁵ lasers,⁶ etc. For the fabrication of nanodevices, crystalline 1D nanostructures are desirable because they can offer better stability and charge-transport properties and thus better optoelectronic performance.⁷ Several methodologies have been developed to prepare 1D organic nanomaterials such as reprecipitation,⁸ self-assembly,⁹ soft/hard templates,¹⁰ and physical vapor deposition.¹¹ Among them, solution-phase self-assembly based on noncovalent intermolecular interactions like hydrogen bonding, π - π stacking, or van der Waals force is one of the most facile and cost-effective methods. Although this method has been successfully used to prepare some crystalline 1D small-molecular-weight organic functional compounds, there are few reports on preparation of 1D crystalline complexes by it.

Eu(TTA)₃phen is a well-known red photoluminescent material with high quantum efficiency and widely applied in electroluminescent devices.¹² However, up to now, little attention has been paid to 1D nanostructures of the complex. Here, we report the preparation of Eu(TTA)₃phen nanobelts by solution-phase self-assembly for the first time.

The synthesis of Eu(TTA)₃phen powders adopted a modified method.¹³ For the preparation of Eu(TTA)₃phen nanobelts, Eu(TTA)₃phen was dissolved in THF to a concentration of 5 mM. Then 4 mL of the solution was injected into 5 mL of high-purity water with stirring. After being stirred for 10 min., the solution was left undisturbed for 8 h to form nanostructures. For detailed experimental and characterization procedure of Eu(TTA)₃phen powders and nanostructures see Supporting Information.¹⁷

Figure 1 shows a typical FE-SEM image of the products. As can be seen from Figure 1, the products consist of a large quantity of nanobelts with smooth surfaces. These nanobelts have a length of up to 60 μ m, a width of 0.7–1.2 μ m, and a thickness of about 120 nm. It should be pointed out that no surfactant, template, or catalyst is needed in the present

preparation system. In fact, other than source materials for Eu(TTA)₃phen, only two solvents (water and THF) were used in the process, thus easily yielding high-purity nanomaterials free from contaminations. As Eu(TTA)₃phen is insoluble in water, practically all Eu(TTA)₃phen molecules are segregated and assembled to form nanobelts in the water.

In order to confirm the composition and purity of the as-prepared nanobelts, element analysis, energy-dispersive X-ray (EDS) spectra, Fourier transform infrared (FTIR) spectra, and weight loss curves were measured. The elemental analysis data show the weight percent of C:N:H is 43.56:2.63:1.72 in the products, which is close to the theoretical weight percent of C:N:H in pure Eu(TTA)₃phen with 43.41:2.81:2.01. The EDS spectrum in Figure S1 indicates that the nanobelts chiefly consist of Eu, C, O, F, and S. The existence of a Si peak originates from silicon substrate, which is used as sample supporter during measurement process. The N element is not observed because of EDX detection limitations. The ratio of Eu:F:S is 0.84:7.21:2.92, which is close to the stoichiometric proportion of Eu:F:S in Eu(TTA)₃phen with 1:9:3. The FTIR spectra of HTTA, phen, and the products are shown in Figure S2. As can be seen from Figure S2, characteristic vibrational absorption peak of carbonyl group at 1659.31 cm^{-1} in HTTA and that of C=N bond at 1616.22 cm^{-1} in phen are red-shifted to 1627.50 and 1599.91 cm^{-1} in the products, respectively. These phenomena suggest that HTTA and phen molecules form a complex with Eu³⁺ ions. Furthermore, the thermogravimetric curve also shows that the complex nanobelts do not contain water molecule and show obvious two-step weight loss (Figure S3). The weight loss for the first and second stages are measured to be 65.4% and 17.1%, which are basically in agreement with theoretical values of Eu(TTA)₃phen to lose three TTA ligand molecules (66.7%) and one phen ligand molecule (18.1%), respectively. This further confirms that the complex nanobelts are pure Eu(TTA)₃phen.

Figure S4 shows an XRD pattern of the as-prepared Eu(TTA)₃phen nanobelts. It can be seen that Eu(TTA)₃phen nanobelts are crystalline in spite of room-temperature prepara-

tion conditions. A distinctive diffraction peak is observed at $2\theta = 26.25^\circ$, corresponding to a d spacing of 3.39 Å. As many previous reports,¹⁴ the d spacing of 3.39 Å is characteristic of an efficient π - π stacking distance, indicating that π - π interaction is a driving force for the self-assembly of the complex into nanobelts.

UV-vis absorption spectra of $\text{Eu}(\text{TТА})_3\text{phen}$ nanobelts show a blue shift, compared to $\text{Eu}(\text{TТА})_3\text{phen}$ molecules dissolved in THF, as shown in Figure S5. It is well known that the formation of H-type aggregates of organic molecules usually leads to a blue shift in the UV-vis absorption band.¹⁵ The ligands of $\text{Eu}(\text{TТА})_3\text{phen}$ may stack via π - π interaction to form H aggregates, which results in a blue shift in the optical absorption band of ligands.¹⁶

It was found that both the initial concentration of $\text{Eu}(\text{TТА})_3\text{phen}$ molecules and solvent change have obvious influence on morphologies of the final products. As can be seen from Figure S6, when 80, 240, and 400 μL of THF solution of $\text{Eu}(\text{TТА})_3\text{phen}$ was injected into 5 mL of water, keeping other conditions unchanged, the resultant products appeared as dendrites, intermixtures of dendrites and short belts, intermixtures of long and short belts, respectively. The smaller $\text{Eu}(\text{TТА})_3\text{phen}$ molecules are in water, the smaller nuclei will be formed. These nuclei are assembled together through diffusion, which results in the formation of dendrites. When the amount of $\text{Eu}(\text{TТА})_3\text{phen}$ molecules is increased by a certain extent, a large number of nuclei are produced in a shorter time, thus leading to $\text{Eu}(\text{TТА})_3\text{phen}$ molecules assembled through π - π interaction in situ. Belt-like structure will be produced under this circumstance. Interestingly, when 80 μL of THF solution of $\text{Eu}(\text{TТА})_3\text{phen}$ was injected into 5 mL of water/ethanol mixtures with a volume ratio of 1:1, only brick-like structure was obtained (Figure S6d). This can be attributed to the polarity difference between water and ethanol, which leads to different interactions between molecules and thus will induce the assembly and stacking of $\text{Eu}(\text{TТА})_3\text{phen}$ molecules in different modes.

Figure 2 shows photoluminescence emission spectra of THF solution of $\text{Eu}(\text{TТА})_3\text{phen}$ and nanobelts at room temperature, respectively. Both nanobelts and THF solution of $\text{Eu}(\text{TТА})_3\text{phen}$ show the same emission peak locations under excitation wavelength of 300 nm, which can be assigned to the $^5\text{D}_0$ - $^7\text{F}_J$ ($J = 0, 1, 2, 3, 4$) transitions of the Eu^{3+} ions. Although at the same concentration, $\text{Eu}(\text{TТА})_3\text{phen}$ nanobelts show approximate two orders of magnitude greater emission intensity than that of THF solution of $\text{Eu}(\text{TТА})_3\text{phen}$. The quantum yield of $\text{Eu}(\text{TТА})_3\text{phen}$ nanobelts (52.1%) is comparable to raw materials (62.2%) and distinctly higher than $\text{Eu}(\text{TТА})_3\text{phen}$ THF solution (6.6%). The photophysical processes of $\text{Eu}(\text{TТА})_3\text{phen}$ molecules in THF solution and nanobelts can be understood as follows. TTA and phen ligands absorb excitation energy and then transfer the energy to Eu^{3+} ions through the so-called antenna effect, which induces the emission of Eu^{3+} ions. In nanobelts, free rotation of the ligands is inhibited and the excitation energy absorbed by the ligands is transferred to Eu^{3+} ions more efficiently, which will enhance luminescence intensity correspondingly.

In summary, crystalline $\text{Eu}(\text{TТА})_3\text{phen}$ nanobelts have been successfully prepared by facile solution-phase self-assembly. In the present system, concentration and solvent changes can alter the self-assembly process of $\text{Eu}(\text{TТА})_3\text{phen}$ molecules and thus

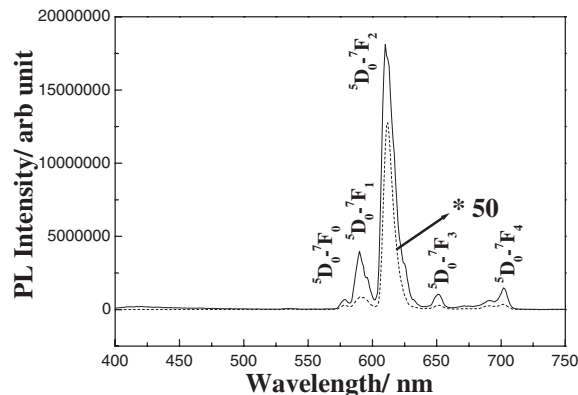


Figure 2. PL spectra of nanobelts (solid line) and $\text{Eu}(\text{TТА})_3\text{phen}$ molecules dissolved in THF at the same concentration (dot line, its emission intensity was magnified 50 times) excited with a wavelength of 300 nm at room temperature.

influence the final morphology of the products. The as-prepared nanobelts with high quantum yield have promising applications in fabrication of optoelectronic nanodevices.

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- 17 Supporting Information is available electronically on the CSJ-Journal Web site, <http://www.csj.jp/journals/chem-lett/index.html>.