

Construction, Characterization and Photoluminescence of Conjugated Micro Porous Polymer Containing Europium (III) Complexes Hybrid Materials

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Abstract. We have synthesized a series of bipyridine-functionalized conjugated micro porous polymers (CMP-Bpy_x) and prepared the first example of a micro porous polymer comprising a luminescent europium complex in the network. This is a new type of red luminescent hybrid materials, named CMP-Bpy_x@Eu(TTA)₃, which were formed by doping [Eu(TTA)₃] into CMP-Bpy_x. The resulting products are amorphous and thermally robust. Further investigation on the luminescence properties of CMP-Bpy_x@Eu(TTA)₃ show that the characteristic luminescence of the corresponding Eu³⁺ through the intramolecular energy transfers from the 2-Thenoyltrifluoroacetone (TTA) to the central Eu³⁺ ions. The property of thermal stability and photoluminescence properties have been enhanced by introducing of conjugated micro porous polymer.

1. Introduction

Bipyridine is a common energy transfer ligand for rare earth complexes[1,2], which satisfies the coordination environment of central rare earth ions[3], and enables the first ligand like β-diketone to transmit energy more effectively[4,5]. However, the simple complex has low light and thermal stability, which severely restricts its practical application. Conjugated microporous polymer(CMP) is a kind of microporous organic polymer consists of a fully conjugated molecular chain with a three-dimensional network structure[6,7]. The material has the optoelectronic properties of some conjugated polymers and provides stable internal porosity, which shows a unique and excellent designable feature[8-13]. Here we selected CMP containing the bipyridine structure to load the rare earth ions. Through the coordination bond, rare earth β-diketone complexes with good fluorescent grafted into microporous channels. A new type of rare-earth/CMP based hybrid material has been constructed. The study of the fluorescence and thermal stability of the materials laid the foundation for the application in electroluminescence.

2. Experimental Section

Synthesis of bipyridine functionalized polymer networks CMP-Bpy_x and CMP-Bpy_x@Eu(TTA)₃.

CMP-Bpy was prepared according to the literature[14]. The general procedure is as follow:
1,3,5-Triethynylbenzene (375mg,2.5mmol),1,4-dibromobenzene (472mg, 2.0 mmol),

5,5-dibromo-2,2'-bipyridine (157 mg, 0.5 mmol), tetrakis-(triphenylphosphine)palladium(0) (30 mg), and copper(I) iodide (10 mg) were dissolved in a mixture of DMF (4 mL) and Et₃N (4 mL). The reaction mixture was heated to 90 °C and stirred for 72 hours under nitrogen atmosphere. The mixture was cooled to room temperature and the insoluble precipitated network polymer was filtered and washed four times with chloroform, water, methanol, and acetone to remove any unreacted monomers or catalyst residues. Further purification of the polymer was carried out by Soxhlet extraction with methanol for 24 hours. The product was dried in vacuum for 24 hours at 70 °C and isolated as fine light yellow powder. Then, CMP-Bpy_x (100mg) was added into a solution of TTA (3 mmol) in 25 mL ethanol, and then the europium chloride (1 mmol in 10 ml of ethanol solvent) was added dropwise to the solution. After stirred for 24 hours, the mixture was cooled to room temperature and the insoluble precipitated network polymer was filtered and washed four times with chloroform, water, methanol, and acetone to remove any unreacted europium complex. The product was then dried under vacuum for 24 hours at 70 °C to give a brown powder.

3. Results and discussion

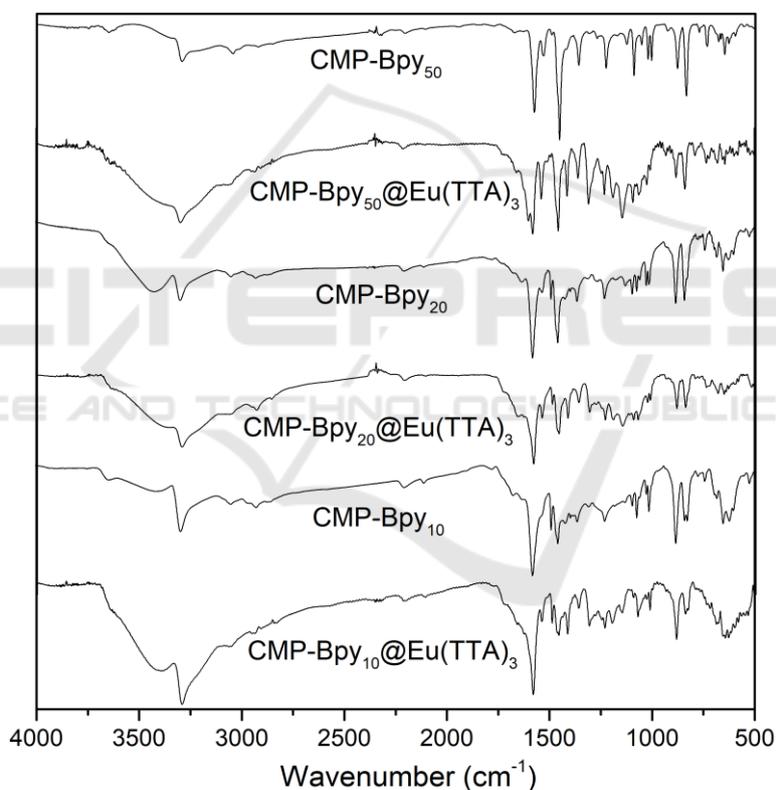


Figure 1. The FT-IR spectra of CMP-Bpy_{10/20/50} and CMP-Bpy_{10/20/50}@Eu(TTA)₃.

It can be seen from the Figure 1 that all CMP-Bpy_x and hybrid materials have peaks at 1576 cm⁻¹ and 1454 cm⁻¹, corresponding to the vibration of aromatic ring skeleton and C-H bond, which means the polymerized polymer networks[7]. As expected, CMP-Bpy₅₀@Eu(TTA)₃ has an obvious wide peak at 1000-1250 cm⁻¹ compared to CMP-Bpy₅₀. Especially the two additional vibration peaks located at 1307 cm⁻¹ and 1091 cm⁻¹ can be ascribed to the characteristic features of C=O and C-F of TTA groups in the europium complexes moiety. This is due to the bipyridine structure is the coordination site of Eu complex. The higher the bipyridine content, the more the TTA will combined with. This means that the rare earth complexes are successfully assembled into the channels through

coordination bonds.

Table 1 lists the specific surface area (BET) and pore volume of CMP-Bpy_x. The BET of CMP-Bpy_{10/20} is larger than 400 m²/g, while the BET of CMP-Bpy₅₀ is lower. The microporous BET and pore volume decreased with the increase of the mole percentage of bipyridine moiety. This may attribute to the negative effect of bipyridine to microporous structure[14]. However, the total pore volume increased with the increase of bipyridine moiety. This is due to the addition of bipyridine disturbed the original microporous structure and lead to the formation of mesoporous and macroporous, which is beneficial to our subsequent load of rare earth complexes.

Table 1. Physical property for polymer networks CMP-Bpy_x.

	S_{BET} [m ² g ⁻¹]	S_{micro} [m ² g ⁻¹](t-plot)	V_{tot} [cm ³ g ⁻¹]	V_{micro} [cm ³ g ⁻¹]
CMP-Bpy₁₀	408.8	206.5	0.24	0.11
CMP-Bpy₂₀	412.1	179.1	0.28	0.09
CMP-Bpy₅₀	345.7	121.9	0.37	0.06

From the N₂ adsorption–desorption curves of CMP-Bpy_x(Figure 2A), it can be seen that all of them are typical I type adsorption isotherm curve for microporous materials. It shows that the outer surface area is much smaller than the inner surface area. For CMP-Bpy₁₀, the adsorption of the probe molecules does not increase as the pressure continues to rise. The curves of CMP-Bpy₂₀ rise slightly, while CMP-Bpy₅₀ increased significantly when the pressure increased. Figure 2B is the pore size distribution curve of CMP-Bpy_x. With the increase of bipyridine content, the number of pores in the micropores and macropores is more, which is consistent with the N₂ desorption curve.

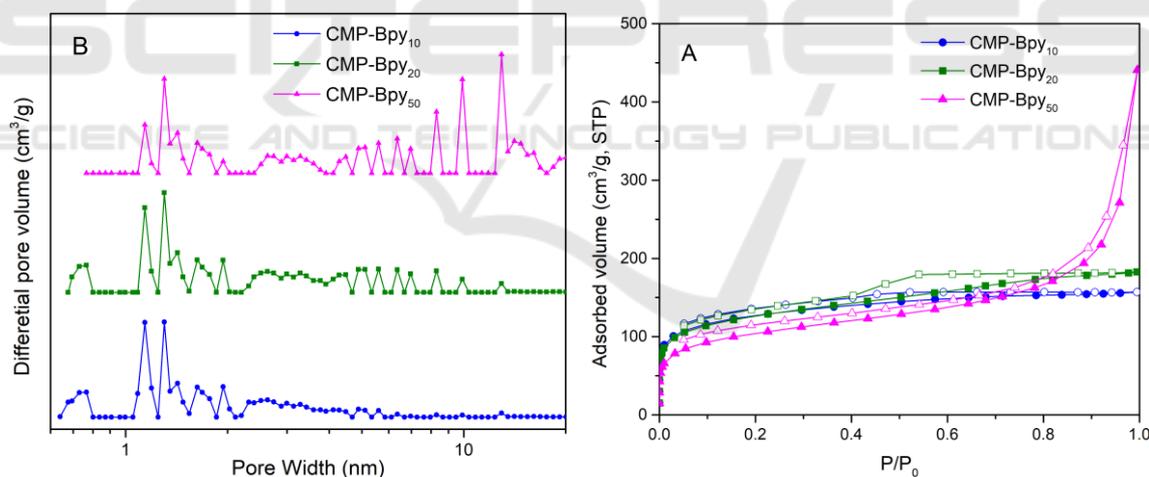


Figure 2. Nitrogen sorption analysis for CMP-Bpy_x (A) and Pore size distribution (B).

Compared the thermogravimetric curve of the hybrid materials CMP-Bpy_x@Eu(TTA)₃ with pure matrix CMP-Bpy_x(Figure 3), it can be seen that the pure CMP materials are stable before 400°C, while the CMP hybrid materials start decomposing at 200°C. Corresponding to the decomposition of organic ligands (TTA) in the micropores, the second stage weightlessness also begins at 400°C, and is the self decomposition of the CMP skeleton. The residual amount of CMP-Bpy_x is higher than CMP-Bpy_x@Eu(TTA)₃ because of the rare earth complex in the excess pore. The results show that the thermal stability of the CMP skeleton has been successfully endow to the hybrid materials CMP-Bpy_x@Eu(TTA)₃, The thermal stability of the rare earth complex has been obviously improved.

This further indicates that the introduction of the stable CMP matrix can improve the thermal stability of the rare earth complexes.

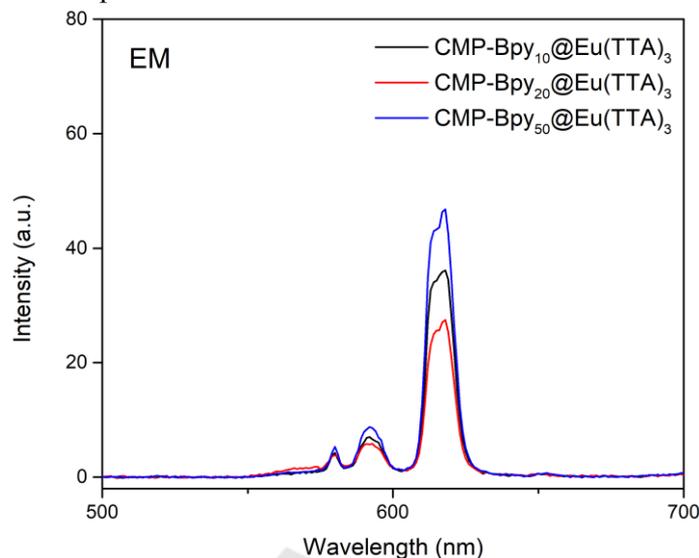


Figure 3. The thermogravimetric curve of $\text{CMP-Bpy}_x\text{@Eu(TTA)}_3$.

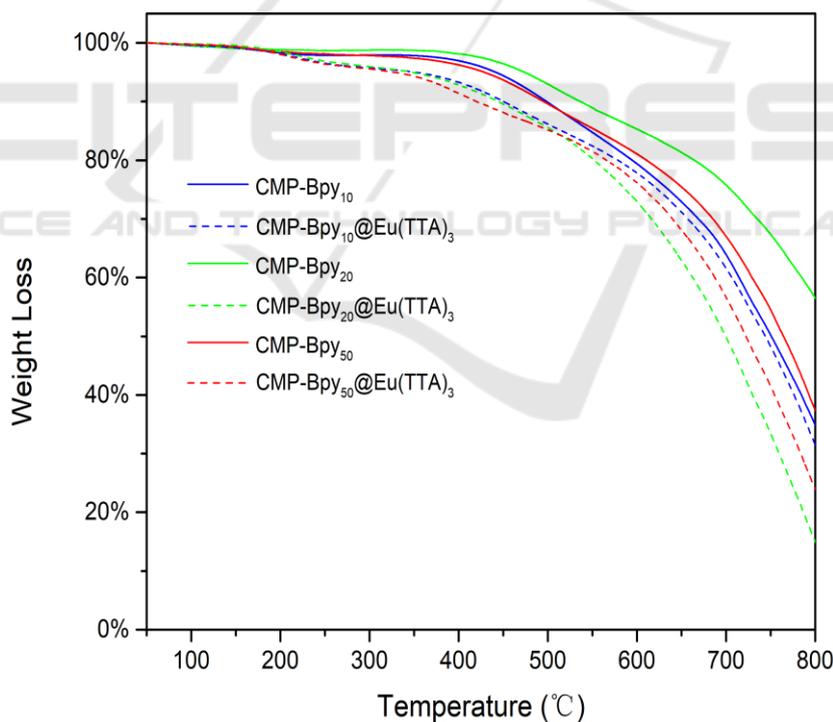


Figure 4. The fluorescent emission spectra of $\text{CMP-Bpy}_x\text{@Eu(TTA)}_3$.

From the fluorescence emission spectra of $\text{CMP-Bpy}_x\text{@Eu(TTA)}_3$ (Figure 4), we can observe that CMP based hybrid materials emit the characteristic emission of Eu^{3+} ions under the excitation of 355nm wavelength. The transition is ${}^5\text{D}_0 \rightarrow {}^7\text{F}_j$ ($j = 0, 1, 2, 3$), corresponding to the wavelengths at 580, 592, 618 and 650 nm, respectively[5]. Among them, the emission of ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition, i.e.,

em = 618 nm, is the strongest emission, accounting for 81% of the total emission intensity, which indicates that Eu^{3+} departed from the center of the inversion symmetry. In order to further study the luminescent properties of hybrid materials. At room temperature, 355 nm and 407 nm were selected as excitation wavelengths to measure the fluorescence attenuation curves of $\text{CMP-Bpy}_x\text{@Eu(TTA)}_3$ and complexes

Table 2. luminescent efficiencies and lifetimes of europium (III) materials.

	I_{01}	I_{02}	I_{02}/I_{01}	τ (ms)	A_r	A_{nr}	η (%)
$\text{CMP-Bpy}_{10}\text{@Eu(TTA)}_3$	10.474	69.854	6.669	0.322	574.974	2603.32	16.24
$\text{CMP-Bpy}_{20}\text{@Eu(TTA)}_3$	8.207	49.473	6.028	0.308	457.293	2793.707	14.07
$\text{CMP-Bpy}_{50}\text{@Eu(TTA)}_3$	4.008	35.025	8.739	0.265	379.835	3398.165	10.05
$[\text{Eu(TTA)}_3] \cdot 2\text{H}_2\text{O}$	46.329	369.41	7.974	0.238	498.718	3706.982	11.86

A_r and A_{nr} are radiative and nonradiative transition rates

$[\text{Eu(TTA)}_3] \cdot 2\text{H}_2\text{O}$ at $^5\text{D}_0$ excited state. The curve shows a single exponential decline, and the fitting curve gets the fluorescence lifetime. The fluorescence lifetime of $\text{CMP-Bpy}_{10}\text{@Eu(TTA)}_3$ is larger than lanthanide complexes $[\text{Eu(TTA)}_3] \cdot 2\text{H}_2\text{O}$. The quantum efficiency of luminescence is further calculated according to the lifetime, as shown in table 2.

4. Conclusions

The complexation of $\text{CMP-Bpy}_x\text{@Eu(TTA)}_3$ with Eu^{3+} ions results in a sharp red-emitting molecular organic-inorganic hybrid material under ultraviolet illumination. Which compared with the pure $[\text{Eu(TTA)}_3] \cdot 2\text{H}_2\text{O}$ rare earth complex material, the property of thermal stability and photoluminescence properties have been enhanced by the introducing of CMP. Ultimately, it is very important to enrich the types of lanthanide luminescent hybrid materials, we believe that these new multifunctional CMP materials will expand the field of lanthanide-based luminescent organic-inorganic hybrid materials.

Acknowledgement

This work was supported by the National Natural Science Foundation of China (21101107, 51173107), the innovation Project of the Shanghai Municipal Education Commission (No.15ZZ076)

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