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Progress of rare earth europium complexes in the field of temperature luminescence sensing

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Abstract:

Rare earth luminescent complex materials, its unique 4f-4f electronic transition, which shows excellent luminous performance, especially the europium complex materials, with temperature dependent luminescent performance of europium complex can achieve high sensitivity, high efficiency of temperature sensing process, can be applied to environmental engineering, energy technology and other fields of temperature measurement and monitoring. This review introduces the research progress of europium complex in temperature luminescence sensing system, summarizes the complex material category and analyzes the influencing factors of temperature response sensitivity, further summarizes the vibration relaxation and energy transfer, and introduces the preparation of europium EVA composite complex and research results in crystal silicon solar cells, for the study of lanthanide metal complexes temperature sensing performance, in order to open the door to the practical application of such materials.

Keywords: Europium complex, Temperature sensing, EVA composite membrane, Lanthanide metal optical ratio meter

1. Introduction

As we all know, researchers have studied the luminous properties of lanthanide metals for decades. Still, the interest of national researchers in the topic has never diminished[1-4]. Lanthanide metals have 4f electronic orbit, a variety of electronic configurations, can provide rich electronic energy levels, therefore, trivalent lanthanide metal ions (Ln^{3+}) Show very diverse optical properties.owing to Ln^{3+}Of 4f orbital by full electron-filled $5s^2 5p^2$Rail field shielding is significant, the transition between 4 fn little affected by the external environment, the relative position between 4 fn level and ground state level remains unchanged, therefore, each lanthanide metal ion has a unique transition level, the emission spectrum shows narrow and sharp band (half peak width is usually less than 10 nm), the luminous spectrum with fingerprint characteristics. The characteristic emission spectra of lanthanide metal ions are diverse, but their chemical properties are basically similar, which is conducive to the introduction of different specific lanthanide metal ions in the same structure system, so as to further enrich the categories of lanthanide metal materials and enhance the practical application value of such materials. This paper mainly introduces the lanthanide europium and terbium metal complex temperature sensing materials, summarizes the preparation method of such materials, temperature response sensitivity factors, inductive vibration relaxation, energy transfer response mechanism, and introduces the research results of optical ratio thermometer in recent years, in order to promote the further development of the field.

1 Luminescence mechanism and process regulation

For molecular luminescent materials, the luminescence process can be simply summarized as the vibration energy level of the ground state molecule excited by external energy, reaching the lowest energy level of the first excited state through non-radiative transition methods such as vibration relaxation and internal conversion, and finally falling back to the ground state, producing light radiation. The return of the molecule in the excited state to the ground state generally goes through two ways, namely radiative and non-radiative transition. The radiation transition process produces optical signals, which are detected by the optical detector. The intelligent optical response molecular materials mainly realize the detection of the external environmental stimulation through the detection of the optical signal transition. The radiative and non-radiative transition processes of excited molecules are in a competitive relationship.[5-7] The non-radiative transition process is usually caused by the vibrational relaxation energy transfer and electron transfer in the separation

system. Studying the influence of external environmental stimulation on the non-radiative transition process is helpful to reveal the response mechanism of optical temperature sensing materials.

1.1 Vibration relaxation

Vibration relaxation refers to the process in which molecules in the excited state collide with the surrounding environment or couple with some vibrations in the molecule, thus leading to non-radiative transition and loss of excitation energy. The loss process of vibratory excitation energy loss in lanthanide metal complex is shown in Figure 1. In 1933, it was first proposed to realize the temperature sensing performance[8]. The temperature sensing system was developed by EU $(tta)_3$(ta: 2-thiophenyl trifluoroacetone, as shown in Figure 2) and deuterated PMMA (polymethacrylate). The temperature response mechanism is the thermal quenching of Eu through a vibrational relaxation process^{3+}excited state level. Generally, numerous C-H bonds or O-H bonds are present in lanthanide metal complexes, which doubling frequency vibration frequency energy with Eu^{3+}The excited state energy is similar, the temperature of the system increases, and the C-H bond vibration is intensified, which can promote the vibrational relaxation process.$Eu^{3+5}D_0 \rightarrow {}^7F_6$(12297 cm-1) can better match the double frequency vibration frequency of C-H (5v 13000cm-1) to promote Eu^{3+}The luminescent quantum yield of the complex decays in response to ambient temperature changes.

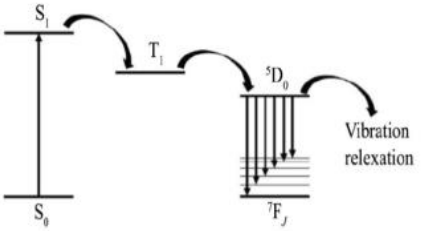


Figure 1 Schematic diagram of vibtation relaxation energy loss process in lanthamide metal complexes

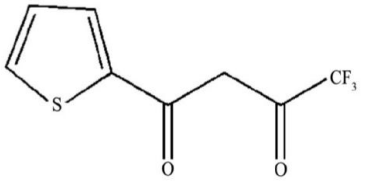


Figure2 Molecular structure of thenoyltrifluoroacetylacetonate

In 2018[9], Cesca et al. used continuous Ar laser to illuminate an orderly arranged silver nanoparticles arrays to heat them by laser-induced plasmonite elements, and used EU $(tta)_3$, As a temperature probe to detect the temperature change. The detection process was mainly performed by measuring Eu (tta a) in PMMA films deposited on the silver nanoparticle $array_3$Temperature-dependent photoluminescence properties, thus determining the degree of temperature increase of the nanoparticle arrays. By this method, it was determined that the maximum increase temperature of the nanoarray surface is 19°C under Ar laser irradiation with a power of 173 mW. The method proved to be a simple and accurate method to probe the actual temperature increase caused by photoinduced plasmon heating.

In 2008[10], Stich et al. proposed a new composite optical material that can simultaneously respond to external pressure and temperature stimuli. The dual-response sensing system is mainly composed of the pair O_2The sensitive Pt porphyrin complex and the temperature-sensitive lanthanide metal complex Eu $(tta)_3$(dpbt) (dpbt: 2- (4 diethylamiobophenyl) -4,6 double (133,5 dimethylpyrazyl) -1,3,5-triazine, as shown in Figure 3). The two components were incorporated into different polymer particles to control their response performance to different external stimuli and avoid mutual interference. The Pt porphyrin complex was encapsulated in polystyrene-propylene dilute nitrile to achieve a wide-range dynamic pressure detection of 105Pa (0.05~2.00). The lanthanide metal complex Eu $(tta)_3$(dpbt) encapsulated in PVC to reduce external oxygen to Eu^{3+}Effect of the luminescence performance. Due to the temperature-sensing component of the lanthanide metal complex Eu $(tta)_3$The luminescence lifetime of (dpbt) is more than ten times higher than that of the pressure-sensing component Pt porphyrin complex, so the two response signals can be distinguished by time-resolved fluorescence imaging to avoid mutual interference. The composite can simultaneously monitor the material surface pressure (or oxygen distribution) and temperature in combination with appropriate time-resolved detection techniques.

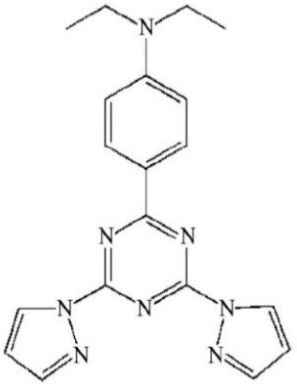


Figure 3 Molecular structure of 2(4-diethylamino-phenyl) 4,6-bis

3,5-dimethylpyrazol-1-yl) -1,3,5-triazine

1.2 Energy transfer

The response to the external temperature is realized by energy transfer, mainly by transferring the excited energy of lanthanide metal ions to other excited energy levels with similar energy, resulting in the change of the luminescence performance of lanthanide metal ions. For example, the Eu $(fod)_3$(Fod: 1,1,2,2,3,3-hepflo-, 7-dimethyl 4,6-ocdione, as shown in Figure 4) Photoreduced Eu was detected in the complex system^{3+}become Eu^{2+}, Demonstrated the existence of a ligand-to-metal charge transfer (LMCT) process in the system, with an energy similar to that of the Eu^{3+} excited state. When the external temperature changes, the Eu^{3+}The excited state level energies are used to realize the LMCT process, Eu^{3+}The luminescence performance changes, eventually achieving the response to ambient temperature changes, as shown in Figure 5.

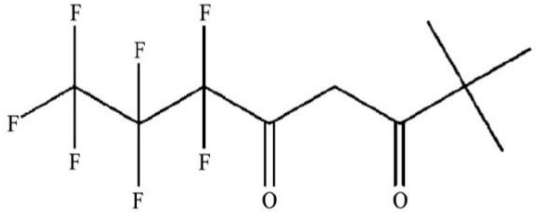


Figure 4 Molecular structure of 1, 1, 1,2,2,3,3-heptafluoro-7, 7-

dimethyl-4,6-octanedionate

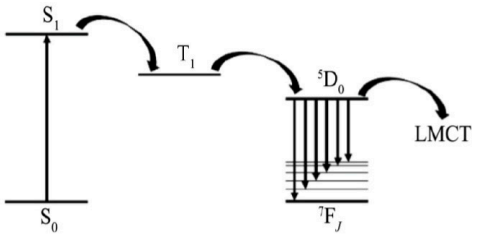


Figure 5 Schematic diagram of energy loss process through LMCT

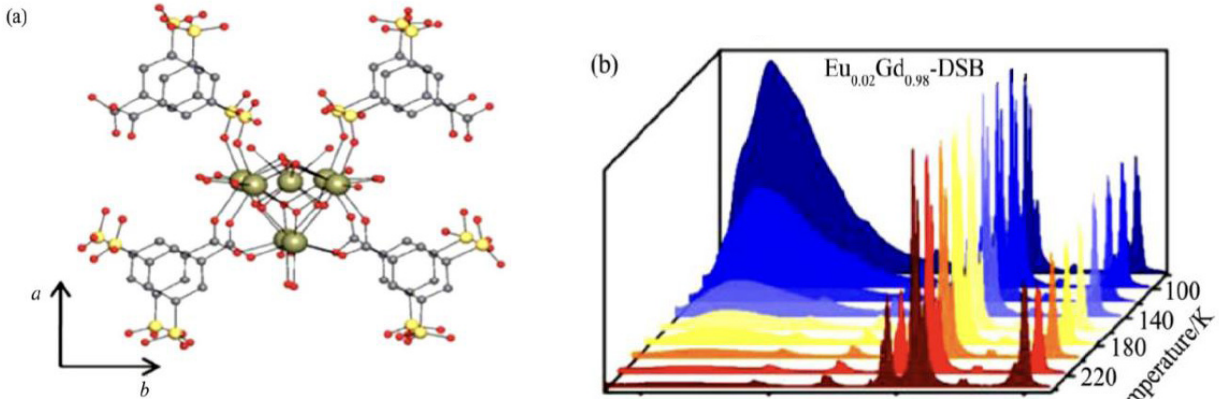
in lanthanide metal complexes

2 Application

2.1 Single lanthanide metal luminescent center optical ratio thermometer

As early as 2013, D-Vries[11] et al. proposed that the organic chromophore was a temperature sensing complex with a ligand and a single lanthanide metal ion (europium or terbium) as a coordinating central metal. The dsb (sb: 3,5-disulfonybenzoic acid) was used as ligand to produce two temperature sensing complexes, Eu 0.02 Gd 0.98 (dsb) and Tb 0.02 Gd 0.98 (dsb) in Figure 6 (a).

among Eu^{3+}And TD^{3+}The luminescence intensity is basically unchanged in the range of 65 to 300 K, but the triplet luminescence intensity of the organic chromophore dsb gradually decays with the increase of temperature in Figure Figure 6 (b), which is caused by the thermal activation transition of the exciton and the intensification of non-radiative energy loss. The intensity ratio at the maximum emission peak of the ligand to the rare earth ions is exponentially dependent on the temperature, and the material is capable of temperature measurement in the range of 10 to 300 K, with a maximum relative sensitivity of 7.14% K-1 at 65 K.



graph 6(a)$[Ln_7(dsb)_4(OH)_9(H2O)_{15}]\cdot 4H_2O$ crystal structure

(b)Eu0.02Gd0.98-dsb Emission spectra at different temperatures

Figure 6 (a)Crystal structure of$[Ln_7(dsb)_4(OH)_9(H_2O)_{15}]\cdot 4H_2O$ (b)emission spectra of Eu0.02Gd0.98-dsbat different temperature

In 2015[12], Cui et al. encapsulated the fluorescent dye flower into the MOF pore of Eu Figure 7 (a) to produce a MOF dye complex with dual luminescence center and developed a new optical ratio thermometer. Dye molecules and Eu energy transfer process, along with the temperature, the luminous intensity ratio and temperature present a linear figure 7 (b), (c), in the physiological temperature range has good temperature sensing performance, simulate physiological conditions, its very low toxicity and good stability, can be applied to the biomedical field. This MOF and dye composite method and a large number of reported Eu lanthanide metal ion complex material significantly different, the method can include organic dyes, various luminous guest molecules to luminous MOF, to expand the luminous wavelength range, to adjust the energy transfer from the luminous guest molecules to lanthanide ions, so as to optimize the double emission complex temperature sensing performance. In 2019, Liu[13] The dye 4-ANA (4-aminonaphthalene dimethimide) dye molecule was encapsulated in Ln-MOF to obtain the complex material of the double luminescence center. The luminescence intensity ratio of the dye and the lanthanide metal luminescence center showed a good linear relationship with the temperature, indicating that the material can also be used as an optical ratiometric thermometer.

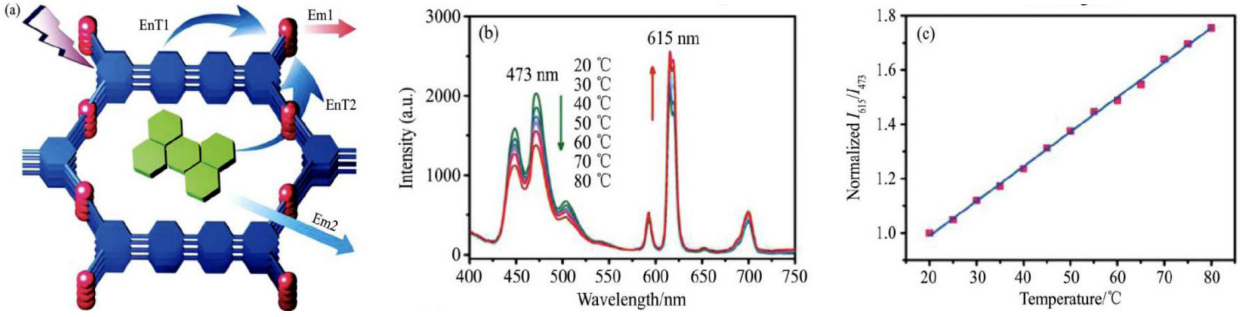


Figure 7 (a)Design of dual-emitting ZJU-88 ∈ perylene com-posite (EnT: energy transfer, Em: emission), (b) e-mission spectra of ZJU-88 ∈ perylene recorded from 20 to 80 C, excited at 388 nm, (c) temperature-de-pendent intensity ratio of Eu^{3+}(615 nm) to perylene (473 nm) and the fitted curve for ZJU-88 ∈ perylene

2020 Outisa[14] et al. introduce a new optical ratiometric thermometer, using two with the same electron level transition ($Eu^{3+5}D_0 \rightarrow {}^7F_2$) The emission peak (613 and 616 nm) of the crystal field sublevel transition, the ratio of the two emission peaks intensity as a function of temperature Figure 8 (a), (b), which is based on $Eu^{3+}$and so on$^5D_0 \rightarrow {}^7F_2$The level transition is highly sensitive to the coordination environment symmetry, and its strength and characteristic peak shape change with the coordination environment. The weakening of the luminescence intensity of the two emission peaks is caused by the intensification of the non-radiative transition caused by the temperature change, while the different degree of the decay is due to the altered coordination environment symmetry caused by the temperature increase. Based on the luminescence characteristics of the characteristic emission peak of lanthanide metal ions, which proposed a novel design idea of lanthanide metal optical ratio thermometer.

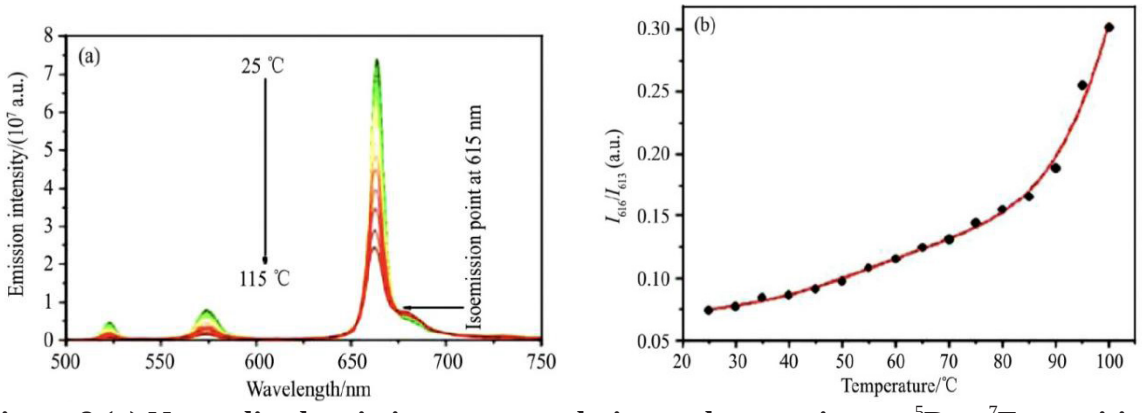


Figure 8 (a) Normalized emission spectra relative to the most intense$^5D_0 \rightarrow {}^7F_2$transition band (from 25 to 110°C with a 5 °Cstep size between each measurement) ,(b) temperature

dependentI_{616nm}/I_{613nm}ratio from 25 to 110 ℃

2.2 Double lanthanide metal luminescence center optical ratio thermometer

In 2012, Cui[15] et al. proposed a novel optical ratio thermometer, based on Eu^{3+}/Tb^{3+}Co-doped MOF system, $Eu_{0.0069}Tb_{0.9931}$-DMBDC (DMBDC is 2,5-dimethoxy-, 4 phthalic acid) Figure 9 (a). Upon excitation of the light source at a 381-nm wavelength, the $Eu_{0.0069}Tb_{0.9931}$-DMBDC simultaneously exhibits $Tb^{3+}$and so on$^5D_4\rightarrow{}^7F_J$(J=6,5,4,3) and the $Eu^{3+}$and so on$^5D_0\rightarrow{}^7F_J$(J=1,2,3,4) Luminescence of the characteristic transition. Because the temperature increase promotes the non-radiative transition energy loss process, the characteristic peak luminescence intensity of Tb-MDBDC and Eu-DMBDC gradually decreases with increasing temperature. However, for the Eu^{3+}/Tb^{3+}The codoped MOF system exhibits temperature-dependent photophysical processes distinct from those of Tb-MDBDC and Eu-DMBDG. In E $u_{0.0069}Tb_{0.9931}$-In the DMBDC structural system, the Tb^{3+}Characteristics of the luminescence peak intensity weakened with increasing temperature, Eu^{3+}The intensity of the characteristic luminous peak increases with increasing temperature Figure 9 (b). At a temperature condition of 10K, 613 nm (Eu^{3+}), And 545 mm (Tb^{3+}) Of the characteristic luminescence peak intensity, but at a temperature of 300K, Eu^{3+}The luminous intensity of the characteristic luminous peak of 613 mm is much higher than that of the other peaks. This is attributed to the Forster energy transfer mechanism, which leads to the removal from Tb under high temperature conditions^{3+}arrive Eu^{3+}Of effective energy transfer, this conjecture can also be demonstrated by luminescence lifetime measurements. It is shown that,$^5D_4\rightarrow{}^7F_5$(Tb^{3+}, 545m) and$^5D_0\rightarrow{}^7F_5$(Eu^{3+}, 613 nm) The characteristic luminescence peak intensity ratio (ITb / I Eu) is linearly related to the temperature change, indicating that $Eu_{0.0069}Tb_{0.9931}$-DMBDC shows very excellent temperature sensing characteristics in a temperature range of 50 to 200 K. Moreover, the corresponding temperature changes are directly observed with adjustable luminous color changes from 10 to 300 K.this type of Eu^{3+}/Tb^{3+}Co-doped MOF system changes with ambient temperature, and the intensity ratio of the two characteristic emission peaks also changes, without further calibration of luminescence intensity, which is an excellent candidate for optical temperature sensor.

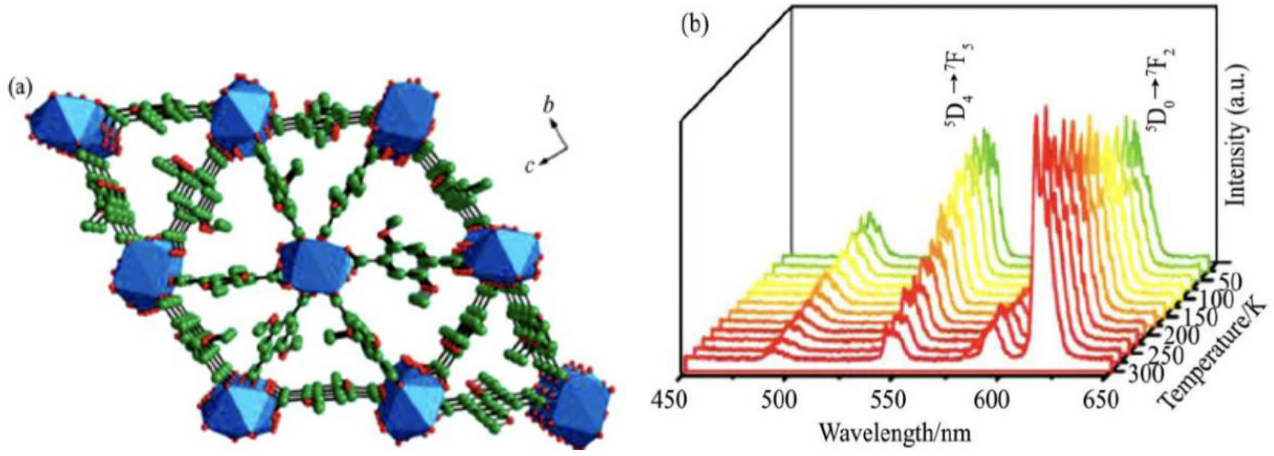


Figure 9 (a) Crystal packing of In-DMBDC viewed along a crystallographic direction (b) emission spectra of E $u_{0.0069}Tb_{0.9931}$-DMBDC recorded between 10 and 300K (excited at 355 nm)

In 2018, Yanagisawa[16] et al. proposed a binuclear Eu with seven coordination configuration with temperature sensing performance$^{3+}/Tb^{3+}$Complex materials. The binuclear complex is composed of a lanthanide metal ion, a tetramethylpediketonate (thd) ligand, and a bidentate phosphonic oxygen (dpbp) ligand Figure 10 (a).Eu^{3+}And Tb^{3+}The luminescence intensity ratio of the characteristic peak is linear with the temperature change, with the temperature response ranging from 100 to 450 K. With the temperature, Eu^{3+}/Tb^{3+}The luminous color of the binuclear complexes is changed from red to green Figure 10 (b).

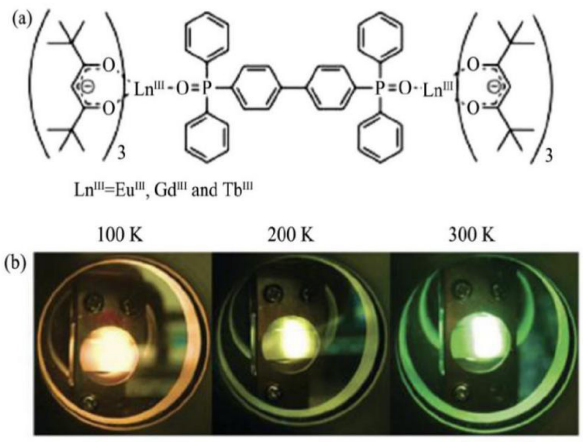


Figure 10 (a)Chemical structure of [Ln2(thd)6dpbp], (b) lu-minescencecolor photos at 100 ~ 300 K

In 2019, Yao[17] et al. prepared a series of hexa-core lanthanide metal complexes by using solvent-thermal and microwave-assisted synthesis methods and using interh-alobenzoic acid as a ligand.Eu^{3+}/Tb^{3+}The co-doped system can show better temperature sensing performance, thanks to the six-core structure, which can effectively enhance the energy transfer ability between metals to better sense the ambient temperature change. In 2019, Pan[18] et al. (successfully synthesized lanthanide metal frame materials with high thermal stability and chemical stability through solvent thermal method, and successfully obtained Eu^{3+}/ Tb^{3+}Co-doped system [$(CH_3)_2NH_2$] $Eu_{0.036}Tb_{0.964}$BPTC (3,3 ′, 5,5 ′) (Figure 25 (a)). The co-doped material has temperature sensing properties in the temperature range of 77 to 377 K, especially showing good linear response in the range of 220 to 310 K, with a maximum relative response sensitivity of 9.42% K-1 at the temperature of 310 K.[19] The luminous color differences at temperatures of 77 and 377 K are distinguishable by the naked eye (Figure 25 (b), (c)). In the same year, Wu et al. covalently modified nano-diamond (NDs) with benzene tetradenic acid (PMA) with lanthanide metal ions, and successfully obtained nano-meter diamond and lanthanide metal luminescent hybrid material ND-PMA-Eu / Tb. In the co-doped composite material, the Tb^{3+} $^5D_4 \rightarrow {}^7F_5$Transition emission with the $Tb^{3+}$$^5D_0 \rightarrow {}^7F_2$The intensity ratio of the transition emission is linear to the temperature, enabling the temperature light response in the range of 77 to 277 K.

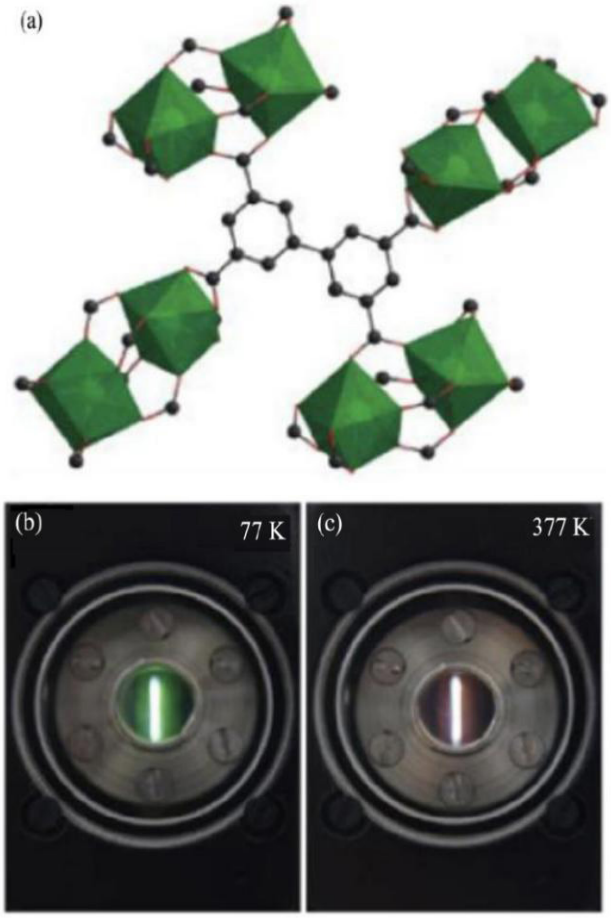


Figure 11 (a) Coordination mode of BPT ligand in[$(CH_3)_2NH_2$] $Eu_{0.036}$T $b_{0.964}$BPTC (b) opticalphotographs of luminescent sample at 77 K (b) and 377 K (c)

3 Conclusion and outlook

Firstly, the luminescence characteristics of lanthanide metal elements are introduced, especially because the excellent luminescence properties of europium complex are suitable for the application of temperature sensing materials. Secondly, it reveals the action mechanism of optical temperature sensing materials, which is essentially the competition relationship between the radiative transition process and the non-radiative transition process of excited molecules under the environmental temperature change, mainly caused by the temperature change affecting the non-radiative transition process. From the perspective of non-radiative transition processes of vibrational relaxation and energy transfer, the response mechanism of temperature sensing materials of lanthanum europium metal complex is explained, and the influence of structure composition, spatial configuration, energy level matching degree

and other factors on the temperature sensing performance is summarized. For complex materials, the frame structure with more firm coordination bonds (such as zirconium metal organic frame) should be selected as the main body, and europium metal ions should be introduced to achieve stability improvement. At the same time, sensitivity is also a key parameter to evaluate the performance of intelligent materials. By comparing the structural characteristics of temperature sensing materials with different mechanisms, the appropriate structural system is selected to adjust the proportion of luminescent components in the structural composition, to achieve the improvement of sensitivity.

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