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ARTICLE TYPE

A ratiometric and colorimetric luminescent thermometer over a wide temperature range based on lanthanide coordination polymer†

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A lanthanide coordination polymer $Tb_{0.957}Eu_{0.043}$cpda was synthesized as ratiometric and colorimetric luminescent thermometer. The high triplet excited state energy of linker enables $Tb_{0.957}Eu_{0.043}$cpda to detect and visualize temperature 10 over a wide range from cryogenic to room temperature (40-300 K).

Metal-organic frameworks (MOFs), also known as coordination polymers (CPs) are very promising multifunctional luminescent materials because of their inherent advantages of both organic 15 linkers and inorganic metal ions, as well as the tailorability in terms of structure, dimension, size and shape.[1] Furthermore, the metal centers, organic linkers, metal-organic charge transfer and guest molecules within porous coordination polymers all can potentially generate luminescence.[2] In particular, the lanthanide 20 metal-organic frameworks have recently been a rapidly developing area due to their unique luminescence properties such as long luminescent lifetime and characteristically sharp line emissions, which span from infrared to blue.[3] In addition, the luminescent intensity of lanthanide ions is very sensitive to the 25 nature of the metal-ion environment, thereby providing an effective means for chemical sensing. Up to now, a variety of luminescent lanthanide coordination polymers have been developed for the recognition and sensing of cations, anions, small molecules, and vapors,[4] however, probes for temperature 30 based on lanthanide coordination polymers have been reported rather rarely.

Temperature is the most frequently measured physical property in both scientific and industrial fields. Conventional temperature sensors are the so-called contact thermometers, in which the 35 measurement of temperature is achieved by heat flow to an invasive probe. Compared with the conventional methods for determining temperature, luminescence-based measurements have attracted much attention because they can be noninvasive, accurate, and work in even strong electromagnetic fields.[5] Such a 40 luminescent method for measuring temperature is mainly based on the temperature dependent luminescence intensity and/or the lifetime of one transition.[6] As measuring the luminescence lifetime requires a relatively long time and post-processing computational treatment, the intensity-based approach is more 45 applicable for real-time temperature measurements.[7] However, the luminescence intensity measurements may suffer from variation of the sensor concentration, excitation power, and the drifts of the optoelectronic system such as lamps and detectors.

Intensity ration, in contrast, is not compromised by these 50 drawbacks, thus is expected to enable more accurate thermal measurements. The ratiometric thermometers based on the intensity ratio of two independent transitions of the same luminophore, instead of only one transition have been developed based on molecular lanthanide coordination compounds, organic-55 inorganic hybrids doped with Eu^{3+} and Tb^{3+} tris(β-diketonate) chelates, and Er^{3+}/Yb^{3+} co-doped up-conversion nanoparticles.[8]

Recently, we have demonstrated the first ratiometric luminescent MOF thermometer, $Eu_{0.0069}Tb_{0.9931}$-DMBDC (DMBDC = 2,5-dimethoxy-1,4-benzendicarboxylate),[9] based on 60 the intensity ratio between emissions of Tb^{3+} at 545 nm and Eu^{3+} at 613 nm. This lanthanide MOF exhibits an excellent linear correlation between temperature and luminescence intensity ratio from 50 to 200 K. Considering that the sensing range could be further expanded by tuning the energy transfer between organic 65 linkers and lanthanides, we selected a N-heterocycle polycarboxylic acid, 5-(4-carboxyphenyl)-2,6-pyridinedicarboxylic acid (H_3cpda), as ligand to construct Eu^{3+}/Tb^{3+} mixed coordination polymer. This ligand exhibits a high triplet excited state energy of 27027 cm^{-1}, enabling the 70 resultant coordination polymer to be an excellent luminescent thermometer over a wide range from cryogenic to room temperature (40-300 K). Furthermore, the significant change of emission color allows the coordination polymer to be a sensitive luminescent colorimetric thermometer for in situ and real-time 75 temperature measurements.

Reacting $Tb(NO_3)_3 \cdot 6H_2O$ or $Eu(NO_3)_3 \cdot 6H_2O$ with H_3cpda yielded colorless rod-like crystals $Tb(H_2cpda)(Hcpda)(H_2O) \cdot 6(H_2O)$ (**Tbcpda**) or $Eu(H_2cpda)(Hcpda)(H_2O) \cdot 6(H_2O)$ (**Eucpda**), respectively.[10] In addition, the Eu^{3+}/Tb^{3+} mixed lanthanide 80 coordination polymer $Tb_{0.957}Eu_{0.043}(H_2cpda)(Hcpda)(H_2O) \cdot 6(H_2O)$ (**$Tb_{0.957}Eu_{0.043}$cpda**) can be readily synthesized by varying the original molar ratios of $Eu(NO_3)_3$ to $Tb(NO_3)_3$ through the same synthetic procedures. The molar ratios of Eu^{3+}/Tb^{3+} in the resulting mixed lanthanide coordination polymer was confirmed 85 by inductively coupled plasma (ICP) analysis, and directly correlated to the amounts of each lanthanide salt used during the corresponding syntheses.

Single-crystal X-ray diffraction analysis revealed that **Tbcpda** crystallizes in the monoclinic space group C2/c (Fig. 1), the 90 H_3cpda ligand exhibits two kinds of coordination modes: one act as bridging ligand, and the other act as terminal ligand. The Tb^{3+} ions is eight-coordinate by two nitrogen atoms and six oxygen
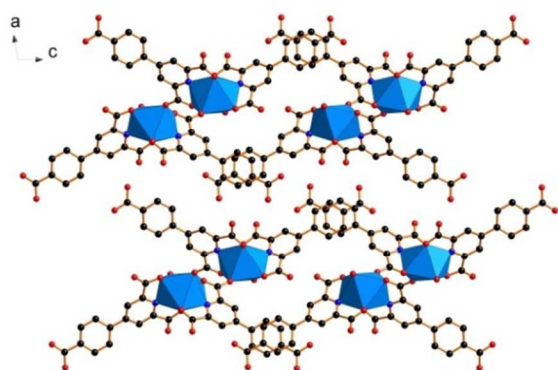
Fig. 1 The crystal packing viewed along the *b* crystallographic direction (Tb, blue polyhedra; C, black; O, red; N, blue; H atoms are omitted for clarity).

atoms, in which six from two tridentate cheated ONO atoms of two H_3cpda ligands, one oxygen atom from neighboring H_3cpda ligand, and another one oxygen atom from coordinated water molecule. The neighboring Tb^{3+} ions are connected by monodentate carboxyl groups of the H_3cpda ligands, generating the zigzag 1D chains along the *b* axis, and then the 1D chains are packed together to form 3D frameworks structure through the π-π interactions and hydrogen bonding interactions. As expected, both **Eucpda** and **Tb$_{0.957}$Eu$_{0.043}$cpda** are isostructural with **Tbcpda**, as confirmed by their single-crystal and powder X-ray diffraction analysis (Fig. S1).

Upon excitation around 335 nm, **Tbcpda** and **Eucpda** display the typical Tb^{3+} and Eu^{3+} emission peaks, respectively, while **Tb$_{0.957}$Eu$_{0.043}$cpda** simultaneously show the characteristic $^5D_4 \rightarrow$ $^7F_{6-4}$ (Tb^{3+}) and $^5D_0 \rightarrow$ $^7F_{1-4}$ (Eu^{3+}) transitions (Fig. S5). No emission bands from the ligand is observed in these compounds, implying efficient energy transfer from H_3cpda ligand to the Tb^{3+} or Eu^{3+} ions. The quantum yield of **Tbcpda** and **Eucpda** are determined to be 15.37 and 14.82%, respectively, suggesting that the lanthanide coordination polymers can be utilized as an excellent candidate for luminescent sensor.

The temperature dependence of the emission spectra (40-300 K) of the mixed coordination polymer **Tb$_{0.957}$Eu$_{0.043}$cpda** is illustrated in Fig. 2. Interestingly, the intensity of the Tb^{3+} luminescence strongly decreases as the temperature increases, while the intensity of the Eu^{3+} emission starts to increase. This luminescence behavior is significantly different from those of **Tbcpda** and **Eucpda**, whose emissions are not temperature sensitive and only shows very few changes over the whole temperature range (Fig. S6 and S7). The temperature-dependent increase of the Eu^{3+} emission could be rationalized by the thermally-driven phonon-assisted Förster transfer mechanism from the Tb^{3+} to Eu^{3+} ions. As shown in Fig. S9, the gradually enhanced emissions of the Eu^{3+} ions in the variable temperature emission spectra of **Tb$_{0.957}$Eu$_{0.043}$cpda** under the 488 nm excitation, which exclusively belongs to the $^7F_6 \rightarrow$ $^5D_4$ transition of the Tb^{3+} ions, clearly indicates that the Tb^{3+}-to-Eu^{3+} energy transfer occurs and enhances with the temperature increases. Further evidence for Tb^{3+}-to-Eu^{3+} energy transfer is demonstrated from the $^5D_4$ and $^5D_0$ emission-decay curves (Fig. S10). The lifetime of $^5D_4$ decrease by approximately 90% as temperature is increased from 15 to 300 K, while the lifetime of
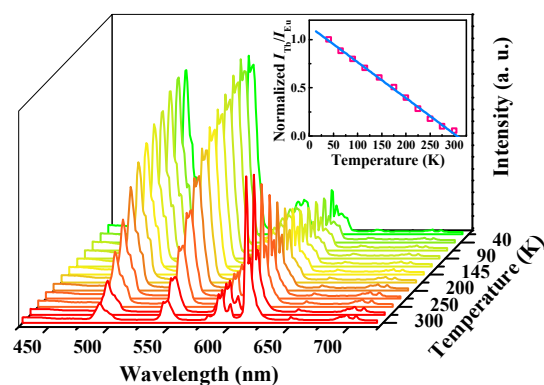
Fig. 2 Emission spectra of **Tb$_{0.957}$Eu$_{0.043}$cpda** recorded between 40 and 300 K excited at 335 nm. Inset: Temperature dependence of the intensity ratio of Tb^{3+} (546 nm) to Eu^{3+} (615 nm) for **Tb$_{0.957}$Eu$_{0.043}$cpda** and the fitted curve.

$^5D_0$ does not display significant decrease. It indicates that some source is feeding the $^5D_0$ level, supporting the nonradiative Tb^{3+}-to-Eu^{3+} energy transfer. A simple definition of the energy transfer efficiency between Tb^{3+} and Eu^{3+} ions can be calculated from the donor lifetime in the presence (τ) and absence (τ_0) of the Eu3+ acceptors:

$$E_{Tb \rightarrow Eu} = 1 - \tau/\tau_0 \qquad (1)$$

As shown in Fig. S11, the energy transfer efficiency from Tb^{3+} to Eu^{3+} is weak at cryogenic region, while strongly enhanced at the elevated temperature, thus resulting in the enhancement of the emission intensity of Eu^{3+} at the cost of the quenching of Tb^{3+} emission with the increase of temperature.

The intensity ratio of two emissions is commonly used as thermometric parameter in ratiometric luminescence temperature sensing. For the mixed coordination polymer **Tb$_{0.957}$Eu$_{0.043}$cpda**, the ratiometric thermometric parameter thermometer can be defined using the ratio of the intensity of the $^5D_4 \rightarrow$ $^7F_5$ (Tb^{3+}, 546 nm) and $^5D_0 \rightarrow$ $^7F_2$ (Eu^{3+}, 615 nm) transitions, allowing the self-referencing measurement of the temperature from the emission spectra. Fig. 2 presents the dependence of the emission intensity ratio (I_{Tb}/I_{Eu}) with temperature. The good linear relation between the I_{Tb}/I_{Eu} and temperature within the range of 40-300 K can be fitted as a function of

$$T = 306.24 - 269.54 I_{Tb}/I_{Eu} \qquad (2)$$

with correlation coefficient of 0.997, indicating that **Tb$_{0.957}$Eu$_{0.043}$cpda** is an excellent luminescent thermometer operative in the range from cryogenic up to room temperature. Although several luminescent thermometers have been available in this range, such a linear response throughout the temperature range from 40-300 K has been rarely reported. This wider temperature response range compared with that of the previously reported **Eu$_{0.0069}$Tb$_{0.9931}$-DMBDC** (50-200 K) could be attributed to the high triplet excited state energy of linker H_3cpda. The triplet energy level of the ligand H_3cpda is estimated to be 27027 cm^{-1} from the low-temperature (77 K) phosphorescence spectra of the Gd^{3+} complex, which is much higher than that of the linker H_2DMBDC (23306 cm^{-1}). The larger energy difference of 6527 cm^{-1} between the excited triplet state and Tb^{3+} emitting level ($^5D_4$, 20500 cm^{-1}) suggests that the energy back-transfer from Tb^{3+} ion to ligand H_3cpda might be efficiently prohibited. This has been confirmed from the variable temperature emission spectra of
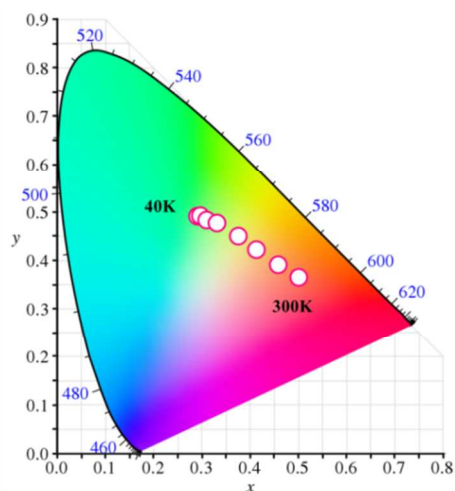
Fig. 3 CIE chromaticity diagram showing the temperature-dependent luminescence color of **Tb$_{0.957}$Eu$_{0.043}$cpda**.

5 **Tbcpda** and **TbDMBDC** (Fig. S6 and S13), in which, the emission intensity of the Tb^{3+} in **Tbcpda** almost remains unchanged with the temperature increases, while the emission in **TbDMBDC** significantly decreases. Due to the restriction of the competing energy back-transfer from Tb^{3+} to ligand H$_3$cpda, the 10 phonon-assisted Tb^{3+}-to-Eu^{3+} energy transfer will be more effective in **Tb$_{0.957}$Eu$_{0.043}$cpda** at the elevated temperature (Fig. S11), thus resulting in the wider temperature sensing range than **Eu$_{0.0069}$Tb$_{0.9931}$-DMBDC**.

In addition, the luminescence color change of 15 **Tb$_{0.957}$Eu$_{0.043}$cpda** makes it especially easy to use as a sensitive luminescent colorimetric thermometer for in situ visualizing the temperature change instantly and straightforwardly over a wide temperature range. As shown in Fig. 3, the temperature-dependent emission spectra are transformed to the Commission 20 International d'Eclairage (CIE) chromaticity diagram coordinates. When the temperature increases from 40 to 300 K, the luminescence color of **Tb$_{0.957}$Eu$_{0.043}$cpda** gradually shifts from green to orange. According to the direct color observation with the naked eye or CCD camera, the environmental temperature can 25 be readily estimated by comparison with the temperature-dependent CIE chromaticity diagram, thus providing a useful tool for the mapping of temperature distribution.

In summary, a novel thermosensitive lanthanide coordination polymer **Tb$_{0.957}$Eu$_{0.043}$cpda** was successfully synthesized by 30 doping Eu^{3+} ions into the isostructural coordination polymer. This coordination polymer exhibits a high emission quantum yield and significant temperature-dependent luminescence. Due to the high triplet excited state energy of linker, the intensity ratio of the $^5D_4$ → $^7F_5$ (Tb^{3+}) to $^5D_0$ → $^7F_2$ (Eu^{3+}) transition can be linearly 35 related to the temperature from 40 to 300 K, enabling **Tb$_{0.957}$Eu$_{0.043}$cpda** to be an excellent candidate for luminescent ratiometric thermometer over a wide range. Furthermore, the tunable luminescence colors from the green to orange from 40 to 300 K allow **Tb$_{0.957}$Eu$_{0.043}$cpda** as a sensitive luminescent 40 colorimetric thermometer to directly map the temperature distribution. The results will provide insights for designing various lanthanide coordination polymers for practically useful luminescent thermometers with tunable response range.

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