This is an Accepted Manuscript, which has been through the RSC Publishing peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, which is prior to technical editing, formatting and proof reading. This free service from RSC Publishing allows authors to make their results available to the community, in citable form, before publication of the edited article. This Accepted Manuscript will be replaced by the edited and formatted Advance Article as soon as this is available.

To cite this manuscript please use its permanent Digital Object Identifier (DOI®), which is identical for all formats of publication.

More information about Accepted Manuscripts can be found in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics contained in the manuscript submitted by the author(s) which may alter content, and that the standard Terms & Conditions and the ethical guidelines that apply to the journal are still applicable. In no event shall the RSC be held responsible for any errors or omissions in these Accepted Manuscript manuscripts or any consequences arising from the use of any information contained in them.
A ratiometric and colorimetric luminescent thermometer over a wide temperature range based on lanthanide coordination polymer†

Yuanjing Cui,* Wenfeng Zou, Ruijing Song, Jiancan Yu, Wenqian Zhang, Yu Yang, Guodong Qian*

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

A lanthanide coordination polymer Tb$_{0.95}$Eu$_{0.043}$cpda was synthesized as ratiometric and colorimetric luminescent thermometer. The high triplet excited state energy of linker enables Tb$_{0.95}$Eu$_{0.043}$cpda to detect and visualize temperature 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 linkers and inorganic metal ions, as well as the tailorable properties in terms of structure, dimension, size and shape. Furthermore, the metal centers, organic linkers, metal-organic charge transfer and guest molecules within porous coordination polymers all can potentially generate luminescence. In particular, the lanthanide 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. In addition, the luminescent intensity of lanthanide ions is very sensitive to the 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, however, probes for temperature 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 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. Such a luminescent method for measuring temperature is mainly based on the temperature dependent luminescence intensity and/or the lifetime of one transition. As measuring the luminescence lifetime requires a relatively long time and post-processing computational treatment, the intensity-based approach is more applicable for real-time temperature measurements. 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 ratio, in contrast, is not compromised by these 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 luminesophore, instead of only one transition have been developed based on molecular lanthanide coordination compounds, organic-inorganic hybrids doped with Eu$^{3+}$ and Tb$^{3+}$ tris(β-diketonate) chelates, and Er$^{3+}$/Yb$^{3+}$ co-doped up-conversion nanoparticles.

Recently, we have demonstrated the first ratiometric luminescent MOF thermometer, Eu$_{0.065}$Tb$_{0.935}$-DMBDC (DMBDC = 2,5-dimethoxy-1,4-benzencarboxylate)$_3$ based on 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 linkers and lanthanides, we selected a N-heterocycle polycarboxylic acid, 5-(4-carboxyphenyl)-2,6-pyridinedicarboxylic acid (H$_2$cpda), 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 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 temperature measurements.

Reacting Tb(NO$_3$)$_3$·6H$_2$O or Eu(NO$_3$)$_3$·6H$_2$O with H$_2$cpda yielded colorless rod-like crystals Tb(H$_2$cpda)(Hcpda)(H$_2$O)$_3$·6(H$_2$O) (Tbcpda) or Eu(H$_2$cpda)(Hcpda)(H$_2$O)$_3$·6(H$_2$O) (Eu$^+$cpda), respectively. In addition, the Eu$^{3+}$/Tb$^{3+}$ mixed lanthanide coordination polymer Tb$_{0.95}$Eu$_{0.043}$cpda (H$_2$cpda)(Hcpda)(H$_2$O)$_3$·6(H$_2$O) (Tb$_{0.95}$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 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 Tb$^{3+}$ cpda crystallizes in the monoclinic space group C2/c (Fig. 1), the H$_2$cpda 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.
atoms, in which six from two tridentate cheated ONO atoms of two H$_2$cpda ligands, one oxygen atom from neighboring H$_2$cpda ligand, and another one oxygen atom from coordinated water molecule. The neighboring Tb$^{3+}$ ions are connected by monodentate carboxyl groups of the H$_2$cpda 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$_{0.95}$Eucpda 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$_{0.95}$Eucpda simultaneously show the characteristic $^5D_4 \rightarrow ^7F_{6,4}$ (Tb$^{3+}$) and $^5D_0 \rightarrow ^7F_{6,4}$ (Eu$^{3+}$) transitions (Fig. S5). No emission bands from the ligand is observed in these compounds, implying efficient energy transfer from H$_2$cpda 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$_{0.95}$Eucpda 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$_{0.95}$Eucpda under the 488 nm excitation, which exclusively belongs to the $^5F_{6} \rightarrow ^7D_{4}$ 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 the temperature is increased from 15 to 300 K, while the lifetime of $^5D_0$ does not display significant decrease. It indicates that some source is feeding the $^5D_0$ level, supporting the nonradiative Tb$^{3+}$ 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 ($\tau$) and absence ($\tau_0$) of the Eu$^{3+}$ acceptors:

$$E_{Tb-Eu} = 1 - \frac{\tau}{\tau_0} \quad (1)$$

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 temperature intensity ratio of two emissions is commonly used as thermometric parameter in ratiometric luminescence temperature sensing. For the mixed coordination polymer Tb$_{0.95}$Eucpda, the ratiometric thermometric parameter thermometer can be defined using the ratio of the intensity of the $^5D_4 \rightarrow ^7F_2$ (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

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

correlation coefficient of 0.997, indicating that Tb$_{0.95}$Eucpda 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$_{0.096}$Tb$_{0.904}$-DMBDC (50-200 K) could be attributed to the high triplet excited state energy of linker H$_2$cpda. The triplet energy level of the ligand H$_2$cpda 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$_2$DMBDC (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$_2$cpda might be efficiently prohibited. This has been confirmed from the variable temperature emission spectra of
...polymer-phonon-assisted Tb→Eu energy transfer will be more effective in Tb$_{0.95}$Eu$_{0.05}$cpda at the elevated temperature (Fig. S11), thus resulting in the wider temperature sensing range than Eu$_{0.065}$Tb$_{0.935}$-DMBDC.

In addition, the luminescence color change of Tb$_{0.95}$Eu$_{0.05}$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 International d’Eclairage (CIE) chromaticity diagram coordinates. When the temperature increases from 40 to 300 K, the luminescence color of Tb$_{0.95}$Eu$_{0.05}$cpda gradually shifts from green to orange. According to the direct color observation with the naked eye or CCD camera, the environmental temperature can 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$_{0.95}$Eu$_{0.05}$cpda was successfully synthesized by doping Eu$^{3+}$ ions into the isosctructural 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 $^5D_{4} \rightarrow ^7F_4$ (Tb$^{3+}$) to $^4D_0 \rightarrow ^4F_2$ (Eu$^{3+}$) transition can be linearly related to the temperature from 40 to 300 K, enabling Tb$_{0.95}$Eu$_{0.05}$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$_{0.95}$Eu$_{0.05}$cpda as a sensitive luminescent 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.

This work was supported by the National Natural Science Foundation of China (Nos. 51010002, 51272229 and 51272231), Zhejiang Provincial Natural Science Foundation of China (No. LR13E020001) and Qianjiang Talent Project (No. QJD1302009)

Notes and references

State Key Laboratory of Silicon Materials, Cyrs Tang Center for Sensor Materials and Applications, Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, China, Tel: +86-571-87952334. E-mail: cuiyj@zju.edu.cn, gdqian@zju.edu.cn

† Electronic Supplementary Information (ESI) available: Experimental details and X-ray crystallographic data. CCDC 970479. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x.


This is a reference to a journal article.