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A Eu/Tb-mixed MOF for luminescent high-temperature sensing

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ABSTRACT

Temperature measurements and thermal mapping using luminescent MOF operating in the high-temperature range are of great interest in the micro-electronic diagnosis. In this paper, we report a thermostable Eu/Tb-mixed MOF **$Eu_{0.37}Tb_{0.63}$-BTC-a** exhibiting strong luminescence at elevated temperature, which can serve as a ratiometric luminescent thermometer for high-temperature range. The high-temperature operating range (313–473 K), high relative sensitivity and accurate temperature resolution, make such a Eu/Tb-mixed MOF useful for micro-electronic diagnosis.

1. Introduction

In recent years, the accurate measurement of temperature has emerging as a key concern in areas such as microelectronics, microfluidics, microoptics, photonics, and nanomedicine [1]. As traditional temperature probes (e.g., thermistors and thermocouples) are not suitable for temperature measurement at molecular scale, luminescence-based thermometers have been developed and attracted much attention due to their non-invasiveness, accuracy, and applicability at micro and nanoscale [2,3]. Temperature dependence of fluorescent properties, such as lifetime, frequency-shift and intensity, have been applied as the metrics in temperature sensing [2,3]. As measuring lifetime or frequency-shift require a relatively long time and additionally computational treatment, the intensity-based measurement is more suitable for the real-time temperature sensing. However, some examples using a single temperature-dependent emission intensity are readily disturbed by the excitation power, variation of the luminophore concentration, and the drifts of the optoelectronic systems, etc. In contrast, the dual-emitting ratiometric measurements, which make use of the intensity ratio of two independent emissions as the ratiometric parameter, can avoid these disadvantages, and are reliable for accurate temperature sensing [2–4]. Recently, a number of mixed lanthanide metal-organic frameworks (Ln-MOFs), with fast response and high relative sensitivity at micro/nano-scales, have been explored and developed as the luminescent thermometers [5–12]. The excellent spatial and temporal resolutions make such Ln-MOF thermometers ideal for temperature measurements or thermal mappings in micro/nano-electronics, as well as detecting the small variations in the resistance-induced local temperature changes that can deteriorate or even fail the systems [13,14].

Ln-MOFs, self-assembled from lanthanide ions with organic ligands, are very promising multifunctional luminescent materials because their building blocks, lanthanide ions, linkers, and guest metal ions or molecules are all potential sources for luminescence [15–26]. Because the luminescence of lanthanide ions (e.g., Tb^{3+} and Eu^{3+}) of certain Ln-MOFs changes considerably with temperature, in the last few years, these materials have been developed as luminescent thermometers, especially in ratiometric temperature sensing based on the intensity ratio of two characteristic transitions (e.g., $^5D_4 \rightarrow {}^7F_5$, Tb^{3+} and $^5D_0 \rightarrow {}^7F_2$, Eu^{3+}) [27]. Although a number of ratiometric Ln-MOF thermometers operative in many temperature regions, such as cryogenic (< 100 K), medium (100–300 K) and physiological (298–328 K), have been reported and present good performances, materials for sensing in high-temperature range (> 375 K) are still rare and worth exploring [5–12].

In order to exploit for Ln-MOFs that can serve as luminescent thermometers and operate in high-temperature ranges, we select 1,3,5-benzenetricarboxylate (H_3BTC) as the linker to construct the Ln-MOFs with Tb^{3+} and Eu^{3+} ions. As has been reported in previous research, such ligand based lanthanide MOF has the rigid framework and superior thermal stability to endure the high temperatures [28], which is a kind of basic premise with regard to the design of luminescent MOF thermometers for high temperature sensing. In addition, the robust framework of this material can support the removal of the organic molecules (e.g. DMF) in the channels, and thus can avoid the vibrational quenching of DMF molecules at elevated temperature [29]. Most importantly, the lowest triplet excite state energy of H_3BTC is calculated to be 26,504 cm^{-1} (Fig. S1), which is much higher

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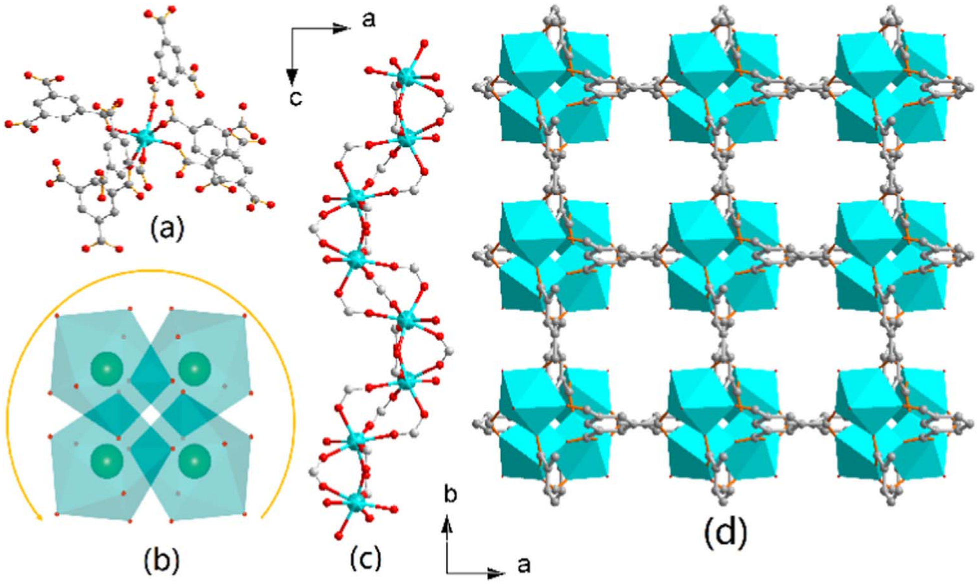

Fig. 1. (a) Coordination environment of Gd^{3+}. (b) Polyhedron drawing illustration over the left-hand helical chain along the *c*-axis. (c) 1 D Gd^{3+}-carboxylate helical chain as the infinite SBU along the *b*-axis. (d) Framework view along the *c*-axis.

than the accepting level of Tb^{3+} and Eu^{3+} ions, thus can effectively prevent the energy-back transfer from Tb^{3+} or Eu^{3+} ions to linker H_3BTC. Based on these concerns, we successfully synthesized the LnMOF **$Eu_{0.37}Tb_{0.63}$-BTC-a**, with high sensitivity, accurate temperature resolution, and excellent repeatability, as a luminescent thermometer for sensing in the temperature range of 313–473 K and might be useful for temperature sensing or thermal mapping in microelectronic diagnosis.

2. Experimental section

2.1. Materials and measurements

All solvents and reagents were commercially available and used without further purification. Thermogravimetric (TG) analyse of the compound was performed on a Netzsch TG209F3 instrument at a heating rate of 10 °C/min from room temperature to 800 °C under N_2 atmosphere. Infrared (IR) spectra were recorded using a Thermo Fisher Nicolet iS10 spectrometer with KBr pallets. Powder X-ray diffraction (PXRD) patterns were recorded in 2θ range of 5–50° on an MAXima_X XRD-7000 diffractometer with Cu Kα (λ=1.542 Å) at room temperature. Inductively coupled plasma (ICP) spectroscopy was carried out on a Thermo IRIS Intrepid II XSP spectrometer. Elemental analyses for C, H and N were recorded on an EA1112 micro-elemental analyser. Room-temperature excitation and emission spectra for the compounds were recorded by a Hitachi F4600 fluorescence spectrometer. The temperature-dependent emission spectra and the luminescence decay curves were obtained on an Edinburgh Instrument F920 spectrometer with a TAP-02 (40–300 °C) temperature control device. Single-crystal X-ray diffraction data of **Gd-BTC** was taken on an Bruker APEX-II diffractometer with an CCD detector using graphite-monochromatic Mo Kα radiation (λ=0.71073 Å) at 293 K. The determination of the unit cell and data collection were performed with Bruker SAINT Program [30]. The structure of **Gd-BTC** was determined by direct methods and refined by the full-matrix least-squares method with the SHELX-97 [31]. Crystallographic data are summarized in Table S1.

2.2. Synthesize of $[Gd(C_9H_3O_6)H_2O]\cdot(H_2O)(DMF)$ (Gd-BTC)

A mixture of H_3BTC (300 mg, 1.43 mmol), $Gd(NO_3)_3\cdot 6(H_2O)$ (645.4 mg, 1.43 mmol) was dissolved in DMF/H_2O (60 mL, 3:1, v/v) in a 100 mL glass vial, and the hydrochloric acid (0.5 mL) had been added, then the glass vial was capped and placed in an oven at 80 °C for 12 h. After slowly cooling to room temperature, colorless crystals were harvested by filtration and washed with DMF several times (73% yield based on H_3BTC). Anal. Calcd for $[Gd\ (C_9H_3O_6)H_2O]\cdot(H_2O)(DMF)$ ($C_{12}H_{14}GdNO_9$): C, 30.44; H, 2.98; N, 2.96. Found: C, 30.02; H, 2.99; N, 2.65. The Tb-BTC and Eu-BTC were synthesized similarly to Gd-BTC except for the use of $Tb(NO_3)_3\cdot 6(H_2O)$ and $Eu(NO_3)_3\cdot 6(H_2O)$, respectively.

2.3. Synthesize of *$Eu_{0.37}Tb_{0.63}$-BTC*

The Eu/Tb mixed MOF can be prepared by using the same synthetic procedure of **Gd-BTC** except for the use of a mixture of $Eu(NO_3)_3\cdot 6(H_2O)$ and $Tb(NO_3)_3\cdot 6(H_2O)$. The molar ratio of Eu^{3+}/Tb^{3+} in the as-synthesized compound **$Eu_{0.37}Tb_{0.63}$-BTC** was correlated with the original molar ratios of each lanthanide salt in the procedure. Anal. Calcd for $[Eu_{0.37}Tb_{0.63}(C_9H_3O_6)H_2O]\cdot(H_2O)(DMF)$ ($C_{12}H_{14}Eu_{0.37}Tb_{0.63}NO_9$): C, 30.50; H, 2.99; N, 2.96. Found: C, 30.95; H, 2.86; N, 3.15.

3. Results and discussion

Solvothermal reaction of $Gd(NO_3)_3\cdot 6(H_2O)$, 1,3,5-benzenetricarboxylate (H_3BTC) and hydrochloric acid in mixed solvents of N,N-dimethylformamide (DMF) and water at 80 °C yielded colorless rod-like crystals of $[Gd(C_9H_3O_6)H_2O]\cdot(H_2O)(DMF)$ (**Gd-BTC**). The formula of **Gd-BTC** was determined based on TG, elemental analysis and Single-crystal X-ray diffraction studies. As shown in Fig. 1 and Table S1, **Gd-BTC** crystallizes in the tetragonal group $P4_322$, and is comprised of the asymmetric unit that consists of one BTC ligand, one Gd atom and one water molecule. The Gd^{3+} is seven-coordinated with six carboxylate oxygen atoms from six H_3BTC ligand and one oxygen atom from the coordinated water molecule, and the coordinated geometry can be described as a distorted pentagonal-bipyramidal (Fig. 1a). Neighbouring Gd^{3+}, at a spatial distance of 4.71 Å, are connected by carbonyl oxygen atoms of H_3BTC ligands to generate a left-hand helical chains along *c*-axis (Fig. 1b, c), eventually forming a condensed 3D framework containing a 6×6 $Å^2$ channel along *c*-axis (Fig. 1d). The **Ln-BTC** MOFs (Eu^{3+}, Tb^{3+}, Gd^{3+}) and the mixed Ln-