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A Highly Sensitive Luminescent Metal-Organic Framework Thermometer for Physiological Temperature Sensing

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Abstract: Thermal sensing and imaging in the physiological temperature range are of great importance for studying physiological processes and treating diseases. Metal-organic frameworks (MOFs) exhibit great promise for developing luminescent thermometers due to their remarkable structural diversities and tunable luminescence properties. Here, we synthesized a series of luminescent mixed-lanthanide MOFs, $Eu_xTb_{1-x}BPT$ (x = 0.019, 0.058, 0.106; H_3BPT = biphenyl-3,4',5-tricarboxylate acid) and adopted powder X-ray diffraction (PXRD), thermogravimetric analysis (TGA) and Fourier transform infrared (FT-IR) to characterize the resulting products. The temperature-dependent photoluminescence emission spectra were recorded to investigate their potential applications in physiological temperature readout. It is found that the intensity ratio of Tb^{3+} to Eu^{3+} is linearly correlated with temperature and the relative sensitivity is higher than 1.5%/°C over the entire physiological temperature range. Furthermore, the temperature-dependent luminescence color emission allows for visual colorimetric temperature measurements. Luminescence lifetime testing and triplet energy level measurement were further conducted to study the mechanism.

Key Words: lanthanide metal-organic frameworks; luminescent thermometer; ratiometric; colorimetric; high sensitivity; physiological temperature; rare earths

1. Introduction

Temperature is a basic physical parameter in a wide range of areas, not only in daily life but also in scientific and industrial fields, and it is significant to precisely monitor and accurately measure temperature.[1-2] When it comes to sensing physiological temperature in living cells or bodies, the luminescent-based method stands out due to its fast response, high sensitivity, good accuracy and minimally invasive or even noninvasive operation.[3-6] Luminescent thermometers detect temperature based on temperature-dependent signals such as luminescent intensity, luminescent lifetime, maximum emission wavelength and luminescent intensity ratio.[7-12] Intensity-based luminescent thermometers suffer from the inaccuracy caused by experimental conditions such as light source power, sample absorption, scatter cross-section, etc.[13,14] Lifetime determination requires more sophisticated instruments and longer testing time, limiting the development of lifetime-based luminescent thermometers.[15] Compared to intensity-based and lifetime-based thermometers, luminescent intensity ratio thermometers are much better because they are self-referenced and easy to operate.[16-19] So far, many luminescent intensity ratio thermometers have been reported.[20-22]

Among various luminescent materials, lanthanide metal-organic frameworks (MOFs) are ideal candidates for developing luminescent thermometers because both their inorganic lanthanide ions and organic ligands can emit temperature-dependent luminescence.[23-25] More importantly, different lanthanide ions can be incorporated into the one framework to construct mixed-lanthanide MOF materials, and any desired lanthanide composition and luminescence intensity ratio can be obtained by tuning the stoichiometry of the starting reactants.[26-28] With these advantages, mixed-lanthanide MOFs open a new pathway for designing novel luminescent self-referenced thermometers. Since the first ratiometric luminescent MOF thermometer $Eu_{0.0069}Tb_{0.9931}$-DMBDC (DMBDC = 2, 5-dimethoxy-1,4-benzenedicarboxylate) was reported in 2012,[29] some excellent mixed-lanthanide MOF thermometers have been achieved in the past few years.[30-33] However, most of them are working in the cryogenic temperature and some reported mixed-lanthanide MOF thermometers operating in the physiological temperature exhibit a low relative sensi-

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