Breathing Europium–Terbium Co-doped Luminescent MOF as a Broad-Range Ratiometric Thermometer with a Contrasting Temperature–Intensity Relationship

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ABSTRACT: Solvothermal reactions of lanthanide salts and a semirigid tripodal H\textsubscript{4}tatab (4,4′,4″-triazine-1,3,5-triyl{s-p-aminobenzoic acid}) ligand in mixed water and N-methyl pyrrolidone (NMP) generated novel breathing MOFs [Ln(tatab)]\textsubscript{1}·solvent (Ln = Eu in 1-Eu, Tb in 1-Tb, Eu\textsubscript{0.015}Tb\textsubscript{0.985} in 1-Eu\textsubscript{0.015}Tb\textsubscript{0.985}). The framework of 1 was contracted upon removal of guests to form partly desolvated [Ln (tatab)]\textsubscript{1}·3.7H\textsubscript{2}O·2.5NMP (1′). Single-crystal X-ray analyses demonstrated that 1 has the breathing ability to spontaneously release guests and maintain the same topology. In contrast to as-synthesized 1, the cell volume of 1′ decreased markedly upon removal of the guests. Different from linear dicarboxylates, the semirigid tripodal tatab ligand is bridged to an inorganic Ln–O chain, limiting the rotation around the O–O axis of carboxylate. The breathing mechanism is based on the flexible C–N–C angles of amide bonds in the tatab ligand, causing a change in the solvent-accessible volume in the framework. Interestingly, the luminescence color of breathing co-doped lanthanide MOF 1′-Eu\textsubscript{0.015}Tb\textsubscript{0.985} is blue-shifted and turned from orange to green with an increase in temperature, which can be attributed to a change in the relative intensity of Tb and Eu emissions, and is quite different from that observed for the reported related compounds. The breathing co-doped lanthanide MOF 1′-Eu\textsubscript{0.015}Tb\textsubscript{0.985} can be applied as a high-sensitivity ratiometric thermometer in a broad temperature from 90 to 300 K.

INTRODUCTION

Metal–organic frameworks (MOFs) have exceptionally high porosities and versatile structural features that allow for their applications in a wide range of areas.\textsuperscript{1–4} Over recent years, breathing MOFs have received intense attention because they can undergo expansion and contraction of the void space in the framework upon application of external stimuli, such as temperature and pressure changes or the inclusion of guest frameworks upon application of external stimuli, such as temperature and pressure changes or the inclusion of guest molecules.\textsuperscript{5–9} Functionally, breathing MOFs show selective, stepwise, reversible, and hysteretic adsorption properties.\textsuperscript{6} Structurally, they exhibit flexibility and unusual dynamic behaviors, which are typically seen in the MIL-53 family, with rhombic channels built from the interconnection of infinite chains of trans-corner-sharing MO\textsubscript{6} polyhedra and linear dicarboxylate ions.\textsuperscript{10–14} The breathing mechanism is generally activated by rotation around the O–O axis of the carboxylate (known as the “kneecap”), which requires an opposite rotation on the opposing side of the rod-like building blocks. On this account, a large number of researchers choose octahedrally coordinated metal ions and linear dicarboxylate ligands rather than tri-topic ligands.

Lanthanide ions show variable coordination numbers and geometries, which, in combination with the tripodal ligand of long arms, may facilitate the formation of novel breathing lanthanide metal–organic frameworks (Ln-MOFs). In particular, Ln-MOFs display unique luminescence properties, such as long luminescent lifetime, large Stokes shifts, characteristically sharp line emissions, and pure emitting colors.\textsuperscript{15–17} Actually, Ln-MOFs have been emerging as a class of very promising luminescence materials and thermometers due to their fast response and high sensitivity.\textsuperscript{18–20} With respect to luminescence thermometers, Ln-MOF luminescence thermometers differ from traditional thermometers and thermocouple thermometers, which have constraints of application at the molecular scale as well as under some special conditions, such as strong electromagnetism. To date, luminescent thermometers of Ln-MOFs have mainly focused on those with single transition emission, and can thus easily be affected by the excitation power, variation in sensors, and drifts of optoelectronic systems.\textsuperscript{21,22} Recently, ratiometric thermometers based on the intensity ratio of two independent transitions from different lanthanides have attracted the attention of researchers due to enhanced sensitivity for accurate temperature sensing.\textsuperscript{23–27} It should be noted that, to date, these kinds of ratiometric thermometers are limited to rigid mixed Eu\textsuperscript{3+} / Tb\textsuperscript{3+} MOFs, where luminescence color redshifts from green of

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Tb to red of Eu with an increase in temperature as a result of energy transfer from Tb to Eu.28–30 Are there abnormalities in the relationship between luminescence and temperature in mixed Eu3+/Tb3+ MOFs? To address this question, we focus our attention on breathing Eu3+/Tb3+ MOFs, as breathing effects of Eu3+/Tb3+ MOFs with temperature may induce some change in host frameworks and guest molecules, which may further induce changes in luminescence arising from energy variations,31 lifetimes,32,33 and the relative emission intensity of Tb, Eu, and organic ligand.

As is well known, to fulfill the luminescent properties of Eu3+/Tb3+ mixed MOF thermometers, the organic linkers need to have a suitable triplet excited state energy in the range of 22 000–24 000 cm−1 to match the energy of the main accepting level of Eu3+(5D1, 24 000 cm−1) and Tb3+(5D4, 21 500 cm−1) (Scheme 1).34,35

In this work, we study the reaction of a tripodal carboxylate ligand, namely, H3tatab (4,4′,4″-s-triazine-1,3,5-triyltris-p-aminobenzoic acid), with Tb(NO3)3/Eu(NO3)3 in mixed solvents of N,N-dimethylformamide (DMF)/H2O with N,N-methyl pyrrolidone (NMP)/H2O, to yield three-dimensional (3D) breathing Ln-MOFs, including single lanthanide 1-Eu and 1-Tb and mixed doped 1-Eu0.015Tb0.985 with one-dimensional (1D) channels. Upon standing or with a change in temperature, the Ln-MOFs show breathing effects involving the removal of guest molecules. Although the breathing Ln-MOFs are isostructural to the reported [Tb(TATAB)2]·4H2O·6DMF,36 the newly synthesized breathing Ln-MOFs, with replacement of the mixed solvent DMF/H2O with NMP/H2O, is more stable. In particular, the crystals that we obtained could be measured at room temperature, whereas the previously reported crystals could only be measured at low temperatures.

Fortunately, mixed Ln-MOF 1′-Eu0.005Tb0.995 can function as a ratiometric thermometer with high sensitivity based on the intensity ratio between emission of Tb3+ at 545 nm and Eu3+ at 614 nm, and can be used in a broad temperature range from 90 to 300 K. In particular, different from reported Eu/Tb luminescent thermometers, such as Eu0.0069Tb0.9931·DMBDC,37 the luminescence color of 1′-Eu0.015Tb0.985 gradually blueshift, rather than redshift, with increasing temperature.

**RESULTS AND DISCUSSION**

**Structural Description.** Primrose yellow single crystals of 1-Eu and 1-Tb as well as co-doped 1-Eu0.015Tb0.985 were obtained by the reaction of H3tatab with Ln3+ at 150 °C for 5 days under solvothermal conditions. After continually optimizing the experiment conditions, a procedure was found that repeatedly yielded large crystals. Single-crystal X-ray diffraction and IR spectra revealed that a series of lanthanide MOFs and co-doped lanthanide MOFs were isomorphous (Figure S1). Here, 1-Eu is taken as an example to describe the structure in detail (Figure 1). 1-Eu crystallizes in the monoclinic space group P21/c, and the asymmetric unit comprises two europium ions and one triply deprotonated tatab ligand. Both Eu(III) ions adopt the same coordination geometry, each coordinated with eight oxygen atoms from two tatab ligands (Figure 1a). The Eu–O distances are in the range 2.289(12)–2.612(11) Å, which are comparable to those in the related europium complexes.39 The Eu(1) and Eu(2) polyhedra are edge-sharing to extend an inorganic Eu–O chain (Figure 1b). The tatab ligand is coordinated to six Eu ions, with six carboxylate oxygen atoms in the μ3-Oη2:η1:η1:η1:η2:η2 mode (Figure 1c). The adjacent chains are further linked by tatab ligands to a 2D layered motif, with the formula of Eu(tatab)0.5 parallel to the c-axis direction, in which semirigid tripodal tatab ligands act as Δ-shaped pillars (Figure 1d). It should be noted that the adjacent two tatab ligands among the Eu–O chains are bridged to an inversion center (Figure 1e). The Eu(tatab)0.5 layers are further pillared by an additional tatab ligand to result in a 3D open framework with parallogram channels along the c-axis direction (Figure 1f). Platon calculations revealed 61.8% potential solvent volume. The smaller angle in the parallogram is ca. 82.7°. The 3D open framework of 1-Eu can be viewed as a cross linkage of two groups of parallel layers.
Different from other ditopic dicarboxylate ligands, tatab ligands are bridged to an inorganic Eu–O chain, limiting the rotation around the O–O-axis of carboxylate.

To further investigate the possible breathing effect, carefully controlled experiments were conducted. The as-synthesized 1-Eu was placed inside desiccators for 48 h to obtain 1′-Eu. The structure of 1′-Eu can also be determined by X-ray single-crystal diffraction. Compound 1′-Eu maintained its original macroscopic morphology and also crystallized in the monoclinic P2_1/c space group. Simultaneously, desolvated 1′ was placed in the mother liquor for two days, and the resolvated sample was tested by XRD. Although the resolvated sample of the majority of reported breathing MOFs showed poor crystallinity, we were able to acquire a resolvated crystal. Compared with primary 1, the cell parameters (a = 29.3277(14) Å, b = 21.7233(18) Å, c = 15.2203(5) Å, α = 90°, β = 103.351(4)°, γ = 90°, V = 9434.6(10) Å³) of the resolvated crystal showed a slight change, which was probably caused by the breathing action of solvent molecules into MOFs pores.

The overall structure of 1′-Eu is a 3D open framework, with parallelogram channels along the c-axis direction, similar to 1-Eu. However, in contrast to as-synthesized 1-Eu, the cell volume decreased markedly upon removal of the guests. The
main structural differences between 1-Eu and 1′-Eu are as follows: (i) The cell parameters were changed from $a = 27.609(3)$ Å, $b = 23.570(3)$ Å, $c = 15.2361(16)$ Å, $β = 104.257(3)^\circ$, and $V = 9609.8(18)$ Å$^3$ in as-synthesized 1-Eu to $a = 32.159(3)$ Å, $b = 16.9564(14)$ Å, $c = 15.0477(12)$ Å, $β = 102.061(2)^\circ$, and $V = 8024.4(12)$ Å$^3$ in 1′-Eu. Compared with the cell volume of as-synthesized 1-Eu, the cell volume of 1′-Eu decreased by 16.4%. (ii) The smaller angle in the parallelogram decreased to 80.7°. (iii) The potential solvent-accessible volume in 1′-Eu decreased from 61.8 to 52.0%. Time-dependent powder X-ray diffraction (PXRD) patterns also confirmed the breathing effect. Mechanically, different from breathing MOFs with linear dicarboxylate ligands, the semirigid tripodal tatab ligand is bridged to the inorganic Eu$^-$O chain to limit the rotation around the O$^-$O-axis of carboxylate. The breathing mechanism is based on the flexible C$^-$N$^-$C angles (127°–133°) of amide bonds in the tatab ligand, resulting in a change in the solvent-accessible volume in the framework. As shown in Figure S2, PXRD patterns of as-synthesized 1-Eu match simulated powder patterns if the measurement was conducted immediately after taking out the as-synthesized sample. The main peaks in PXRD patterns will shift to a higher angle if the sample stood in air for some time and was then measured. The PXRD patterns will not change after standing for 3 days, indicating the formation of a stable desolvated structure. Simultaneously, we conducted thermogravimetric analyses (TGA) measurements in air at a heating rate of 10°C min$^{-1}$ (Figure S3). The number of solvents within 1-Eu cannot be determined from elemental analysis and TGA measurements, as as-synthesized 1-Eu loses solvents very quickly at room temperature. Despite the larger void indicated by the structure, isothermal adsorption measurements did not show permanent porosity, even though many activation conditions were created.

**Luminescence Properties.** To determine whether the tatab linker is an excellent antenna chromophore for sensitizing the lanthanide ions, especially Eu$^{3+}$ and Tb$^{3+}$ ions, the luminescence excitation and emission spectra of solid 1′-Eu, 1′-Tb and free ligand were recorded at room temperature. As mentioned before, as-synthesized Ln-tatab MOFs will desolvate and induce a breathing effect upon standing in air, and thus the as-synthesized crystals were allowed to stand in air for 3 days before luminescent measurements to eliminate the possible influence of guests. The tatab ligand displayed emission peaks of 402, 446, 467, and 517 nm under excitation at 356 nm, which can be attributed to the π$^-\π^*$ transitions (Figure S4). Upon excitation at 381 nm, 1′-Eu displayed emission peaks of the tatab ligand and the characteristic red emissions at 591 and 615 nm, which can be attributed to $5D_0 \rightarrow 7F_j$ ($j = 1, 2$) transitions of Eu$^{3+}$ ions (Figure S5). Simultaneously, 1′-Tb, after excitation at 356 nm, displayed characteristic green luminescence in the narrow emission bands at 488, 543, 583, and 622 nm, ascribed to $5D_{4} \rightarrow 7F_{J}$ ($J = 6−3$) transitions of Tb$^{3+}$ ions (Figure S6). Different from 1′-Eu species, no emission of tatab was observed in 1′-Tb, indicating the energy transfer from tatab to Tb ions. For co-doped mixed lanthanide MOF 1′-Eu$_{0.015}$Tb$_{0.985}$, characteristic emissions for both Eu$^{3+}$ (614 nm) and Tb$^{3+}$ (545 nm) were observed under the excitation at 342 nm (Figure S7).

The temperature-dependent photoluminescence properties of the Ln-MOFs were investigated both in terms of intensity and lifetime to establish their potential as luminescent...
thermometers. In Figure 2a,b, the luminescent intensity of 1’-Eu decreases gradually with an increase in temperature from 90 to 300 K, whereas the luminescent intensity of 1’-Tb does not show an obvious change. It should be noted that emission of tatab did not occur for 1’-Tb in the entire temperature range measured, implying quite efficient energy transfer from tatab to Tb[3+]. All characteristic 5D4→7F6,4 (Tb[3+]) and 5D0→7F1,4 (Eu[3+]) transitions were decreased in the doped mixed lanthanide 1’-Eu0.015Tb0.985 from 90 to 300 K (Figure 2c), with the rate of decrease of Eu[3+] (614 nm) being faster than that of Tb[3+] (545 nm), especially in the range of 230–300 K. Such a decreasing trend can be seen from the integrated intensity (Figure 2d).

To further explore the relationship between the sensitivity of temperature, temperature and the integrated intensity ratio of Tb[3+] (545 nm) to Eu[3+] (614 nm) for 1’-Eu0.015Tb0.985 are plotted, which shows a nonlinear relationship (Figure 3).

Figure 3. Temperature dependence of the integrated intensity ratio of Tb[3+] (545 nm) to Eu[3+] (614 nm) for 1’-Eu0.015Tb0.985 (black squares), and temperature dependence of the integrated intensity ratio of Tb[3+] (545 nm) for 1’-Tb (red circle). Fitted curve of the integrated intensity ratio for 1’-Eu0.015Tb0.985 from 230 to 300 K (inset).

The temperature-dependent luminescence intensity slightly decreased from 1.8 to 1.0 in the range of 90–300 K. In contrast, co-doped MOF 1’-Eu0.015Tb0.985 showed a converse and more sensitive change trend. The emission intensity ratio of 5D4→7F5 (Tb, 545 nm) to 5D0→7F2 (Eu 614 nm) transition for 1’-Eu0.015Tb0.985 approximately to 1.2 and remains constant in the range 90–220 K and then rapidly increased to 3.2 at the highest measured temperature of 300 K. The temperature can be linearly related to the integrated intensity ratio for 1’-Eu0.015Tb0.985 from 230 to 300 K, and the correlation coefficient is R2 = 0.996, indicating that 1’-Eu0.015Tb0.985 is an excellent luminescent thermometer.

\[ T = 188.4 - 40 \frac{I_{Tb}}{I_{Eu}} \] (1)

More importantly, the temperature-dependent luminescence color of 1’-Eu0.015Tb0.985 gradually blueshifted from orange to green with an increase in temperature from 90 to 300 K, which makes it especially easy to use as a sensitive luminescent colorimetric thermometer for straightforward in situ visualization of the temperature change (Figure 4). Also, the photograph of luminescent 1’-Eu0.015Tb0.985 at different temperatures was collected (Figure S8). On the basis of the Commission Internationale d’Eclairage (CIE 1931) chromaticity diagram, the corresponding CIE coordinates change from (0.4486, 0.4896) at 90 K to (0.3261, 0.5213) at 300 K.

Figure 4. (a) Photograph of luminescent 1’-Eu0.015Tb0.985 at 90 K (left) and 300 K (right) after excitation at 342 nm. (b) CIE chromaticity diagram showing the luminescence color of 1’-Eu0.015Tb0.985 at different temperatures.

To better understand the mechanism, the lifetimes of the excited states 5D4(Eu[3+]) and 5D0(Tb[3+]) for these luminescent MOFs at different temperatures were monitored at 614 and 545 nm. With an increase in temperature from 90 to 300 K, the lifetimes for 5D4 in 1’-Eu and 5D0 in 1’-Tb decreased by approximately 50 and 30%, respectively. The lifetimes of 5D4(Tb[3+]) and 5D0(Eu[3+]) not only changed with temperature but also changed with doping of different lanthanide ions. As shown in Table 1, co-doped 1’-Eu0.015Tb0.985 exhibits a longer 5D4(Tb[3+]) lifetime than 1’-Tb, but a shorter 5D0(Eu[3+]) lifetime than 1’-Eu at a given temperature.

**CONCLUSIONS**

In summary, the organic ligand 4,4’,4-s-triazine-1,3,5-triyltri-p-aminobenzoic acid was selected to synthesize new three-dimensional breathing MOFs, which contract framework through losing guest molecules. Interestingly, we found an abnormal blueshift of luminescence color from orange to green with increasing temperature in Eu/Tb-co-doped 1’-Eu0.015Tb0.985, quite different from the redshift in related compounds. The breathing co-doped lanthanide MOF 1’-Eu0.015Tb0.985 can be applied as a high-sensitivity ratiometric thermometer in a broad temperature from 230 to 300 K. At present, the exact reason for the blueshift in our compound instead of a redshift in the related compounds is not clear. However, we speculate that this interesting phenomenon may arise from a minor change in the energy level in our compound induced by interactions between guest molecules and the host framework. The experimental result is seen to repeat; however, the exact reason could be linked to the appearance of more complexes of blueshift. A comparison of their crystal and electron structures should be performed in the future.
**EXPERIMENTAL SECTION**

Materials and Physical Measurements. All reagents and solvents were acquired from a commercial source and used as received without further purification. The Fourier transform infrared (FT-IR) spectra were recorded as KBr discs on the PerkinElmer Spectrum BX FT-IR spectrometer in the range 400–4000 cm⁻¹. The thermogravimetric analyses (TGA) were performed using the SETARAM LABSYS equipment at a heating rate of 10 °C/min under an air atmosphere. Powder X-ray diffraction (PXRD) data were determined by a Bruker D8 ADVANCE diffractometer for Cu Kα radiation (λ = 1.5418 Å). Steady and temperature-dependent fluorescence spectra were investigated on an FLS920 fluorescence spectrophotometer, equipped with a continuous Xe-900 xenon lamp and an F900 microsecond flash lamp as the excitation light source. Temperature control from 90 to 300 K was carried out by a Janis closed cycle refrigerator system. Because desolvation can induce a breathing effect of 1, as-synthesized crystals were allowed to stand in air for one week to ensure desolvation and formation of a stable structure. Inductively coupled plasma (ICP) spectroscopy was performed on a PerkinElmer Optima 8000 DV ICP. The Eu/Tb ratio of Euₐ₀.₀₁₅Tb₀.₉₈₅ was determined by ICP analysis, in agreement with the original molar ratio of Eu³⁺/Tb³⁺ in the starting chemicals.

**Synthesis of [Eu(tatab)]·Solvent (1-Eu) and [Tb(tatab)]·Solvent (1-Tb).** A mixture of Ln(NO₃)₃·6H₂O (0.18 mmol, Ln = Eu, Tb) and H₃tatab (0.027 g, 0.06 mmol) in 6 mL of the mixed solvent of N-methyl pyrrolidone (NMP) (3 mL) and H₂O (3 mL) were stirred for 30 min at room temperature, and then sealed in a 15 mL Teflon-lined stainless autoclave. This was maintained at 150 °C for 5 days. After the mixture was slowly cooled to room temperature and filtered, yellow rodlike crystals of 1-Eu and 1-Tb were obtained in the yield ca. 50% based on H₃tatab. Due to the gradual removal of guests, the result of elemental analyses is precise and thus the IR (KBr pellet, cm⁻¹) for 1-Eu: 3420(s), 2927(w), 2855(w), 1672(m), 1589(m), 1529(m), 1452(m), 1387(vs), 1331(w), 1277(w), 1200(s), 1183(m), 1120(w), 855(m), 821(w), 772(w), 526(m), 480(m). For 1-Tb: 3420(s), 2921(w), 2855(w), 1639(m), 1595(m), 1551(m), 1452(m), 1397(vs), 1315(s), 1271(w), 1195(s), 1129(m), 1118(w), 860(m), 822(w), 773(w), 521(m), 482(m).

**Synthesis of [Eu₀.₀₁₅Tb₀.₉₈₅(tatab)₂]·Solvent (1-Eu₀.₀₁₅Tb₀.₉₈₅).** The synthesis of the mixed-lanthanide compound 1-Eu₀.₀₁₅Tb₀.₉₈₅ was carried out following the above procedure, except for the use of a mixture of Eu(NO₃)₃·6H₂O and Tb(NO₃)₃·6H₂O instead of pure Ln salts.

**Synthesis of [Ln(tatab)]·3.7H₂O·2.5NMP 1′.** As-synthesized 1 was placed in desiccators for 48 h to obtain 1′, during which a yellow crystalline rodlike structure remained. Anal. Calcd (%) for 1′-Eu: C, 53.48; H, 5.53; N, 10.25. Found: C, 53.50; H, 5.23; N, 10.70.

**Single-Crystal Structure Determination.** The crystallographic data were collected on an Agilent Technologies Gemini Eos diffractometer at room temperature using Mo Kα radiation (λ = 0.71073 Å). The program SAI1NT was applied for integration of the diffraction profiles, and absorption corrections were used based on the SAD ABS program. All of the structures were solved by direct methods, and were refined anisotropically with the full-matrix least-squares technique using the Olex2 programs. All nonhydrogen atoms were refined anisotropically. H-atoms on the ligand were placed in idealized positions and refined isotropically with fixed thermal factors.

Initially, we attempted to refine the structure as best as possible, but failed, despite the presence of middle-sized cells and strong diffraction. During data collection, the change from 9610 to 8024 Å³ in 16.5% of the cells indicates a breathing effect of the titled compounds. The crystal data and details of the data collection are presented in Table S1, whereas selected bond lengths and bond angles are presented in Tables S2 and S3.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b00199.

Tables of crystal data, bond distances and angles, tables of lifetime data, ICP, PXRD, IR, TGA, excitation and emission spectra, phosphorescence spectrum, and CIE chromaticity diagram (PDF)

Crystallographic data (CIF)

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**Notes**

The authors declare no competing financial interest.

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