# Europium(III)/Terbium(III) Mixed Metal-Organic Frameworks and Their Application as Ratiometric Thermometers

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ABSTRACT The ability to engineer on a molecular level luminescent metal-organic frameworks (MOFs) is a powerful tool for the design of well-performing rational, that is self-referencing, temperature sensors. Lanthanide based MOF stand out as luminescent temperature sensors due to the high luminescence intensity and sharp emission lines of the lanthanides. The use of two different lanthanide cations incorporated into the same MOF structure is supposed to allow for a rational temperature sensing. Here, we present series of mixed-metal  $Eu_xTb_{(1-x)}BTC$ , in which the metal ions are homogeneously dispersed, as demonstrated by <sup>1</sup>H solid-state NMR spectroscopy. The  $Eu_xTb_{(1-x)}BTC$  series shows controllable luminescent properties, which depend on the solvation of the lanthanide. The two MOFs in the series with the lowest Eu content,  $Eu_{0.04}Tb_{0.96}BTC$  and  $Eu_{0.02}Tb_{0.98}BTC$ , are suitable candidates for rational temperature sensing in the range between 200 to 270 K and 280 to 330 K.

#### Introduction

In the field of chemical sensing, metal-organic frameworks (MOF) have attracted much attention as they combine the advantages of high surface areas and pore volumes, crystallinity with tuneable structures and functionalities.<sup>1,2</sup> Thus, MOFs have found application in easy-to-read optical sensors,<sup>3–5</sup> as well as in electrochemical sensing<sup>6,7</sup> and fluorescent sensing.<sup>2,8–11</sup> MOF-based fluorescence sensors stand out compared to other materials due to their modular synthesis enabling to adjust the MOF structure and chemical composition and, thus, to tailor its properties. This has in the past allowed to design fluorescence sensors with high target selectivity as well as high sensitivities and low limit of detection. MOF-based fluorescence sensors have found application in various fields, including toxic metal ion detections in

wastewater, gas and volatile organic compounds detection but also for determination of physical properties such as pH, humidity and temperature.<sup>2,8–11</sup>

To allow for ratiometric sensing, that is self-calibrating sensing without the use of an external reference, at least two different luminescent centres are required.<sup>10</sup> This can include two different metal complexes, e.g. two different lanthanides, two QDs or a combination of a QD and a metal complex. Lanthanide-based MOFs are attracting increasing attention due to the high luminescence intensity and sharp emission lines of the lanthanides.<sup>8,12</sup> Thus, from the two or more transitions originating from the different emissive centres within the same material, the sensor signal is determined optically as the ratio between the probe-dependent emission intensities. In case of temperature sensing, the nature of the MOF, i.e. the metal and organic linker combination, mainly determines the temperature range which can be accurately measured. However, as ratiometric temperature sensing might offer large potential as an in situ probe to detect local temperature changes during a given application, e.g. a catalytic reaction or an adsorption process. Precise understanding of the temperature sensing under different conditions is required. However, though it is known that the luminescence in LnBTCs strongly depend on the conditions, e.g. the presence of a solvent.<sup>13–15</sup> Systematic studies to enable understanding the interplay between the MOF material and its functional environment are yet rare. So far, it has been postulated that due to intermolecular interaction forces between the BTC linker - from the dispersed MOF - and the solvent, relaxation of excited BTC states occurs instead of energy transfer from excited BTC states to the luminescent Ln centers.<sup>15</sup>

With regard to particle size and shape, most of the pure Ln-containing MOFs known show a preferred crystallization along one crystallographic direction leading typically large needle-shaped crystals.<sup>16–18</sup> While this is very attractive for crystal structure determination, it may hamper their application in areas where size becomes important, such as in contrasting agents in bio-imaging or in thin films. A prominent technique to control the size and shape of MOF

crystals is the use of modulators. In their seminal report, Guo *et al.* reported the use of sodium acetate (NaOAc) as a suitable capping agent to reduce the particle size without affecting the crystal structure and properties of LnBTC MOFs.<sup>19</sup> While the original protocol allowed for the synthesis of rod-like LnBTC of several tenths of  $\mu$ m in length,<sup>8,19</sup> the protocol reported by Guo *et al.* lead to the synthesis of almost spherical particles with diameters below 100 nm. Those LnBTC (nano)particles have found wide application in luminescent sensing, including small molecule detection,<sup>14,20</sup> and ratiometric temperature sensing<sup>21</sup>, or in luminescent thin films.<sup>19,22,23</sup>

Here we report the investigation of the ratiometric temperature sensing in a series of mixed europium and terbium BTC MOFs, labelled as  $Eu_xTb_{(1-x)}BTC$ . Using the NaOAc-modulator approach, the  $Eu_xTb_{(1-x)}BTC$  series was obtained as nanoparticular systems, enabling their use not only in the dry solid state, but also dispersed in various solvents in the colloidal state. Temperature sensing was established on dry powders of  $Eu_{0.04}Tb_{0.96}BTC$  and  $Eu_{0.02}Tb_{0.98}BTC$ . Finally, we will show that an extension towards rational temperature sensing in the presence of a solvent is feasible using the pure EuBTC and TbBTC as model compounds dispersed in ethanol.

#### **Experimental Section**

#### **Materials and Methods**

Eu(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (Thermo Scientific, 99.9%), Tb(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (Thermo Scientific, 99.99%), 1,3,5-benzene tricarboxylic acid (H<sub>3</sub>BTC, Alfa Aeser, 98%), *N*,*N*-dimethylformamide (DMF, Merck, 99.5%), NaOAc (Merck, 99%) and ethanol (Merck, >95%). All chemicals were used as supplied without further purification.

Powder x-ray diffraction (PXRD) patterns were collected on a PANalytical Emryrean series 2 in Bragg-Brentano geometry using CuKα radiation at 20 angles between 2 and 50°. Thermogravimetric analysis (TGA) of powder samples was measured on a Hi-Res TGA 2950 Thermogravimetric Analyzer (TA Instruments) in the temperature range from room temperature to 700 °C with a heating rate of 2 K/min in synthetic air. Inductively coupled plasma optical emission spectroscopy analysis was done using an SPECTRO Ciros-CCD. IR spectra were recorded using a JASCO FT/IR-4100 in attenuated total reflectance geometry (ATR, resolution 2 cm<sup>-1</sup>, 64 scans), Photoluminescence (PL) spectra of the suspensions were recorded using a fluorescence spectrophotometer (Horiba Fluorolog) in the temperature range of -20 to 50 °C. PL spectra of the solid samples were recorded using a JASCO Spectrofluorometer FP-8500 (λ<sub>ex</sub> = 256 nm). Scanning electron microscopy (SEM) images were obtained on a Carl Zeiss Gemini Ultra 55. Dynamic scanning calorimetry was recorded using a NETZSCH DSC 204F1 Phoenix equipped with a liquid nitrogen dewar. Samples were filled into Al pans, closed with an Al lid and analysed between -30 and 100°C with a heating/cooling rate of 2 K/min.

<sup>1</sup>H solid state NMR spectra were collected on a Varian 500 NMR spectrometer (<sup>1</sup>H resonance frequency at 499.86 MHz) equipped with a 1.6 mm probe at a spinning frequency of 30 kHz. Prior to NMR measurements, all samples were activated overnight at 250 <sup>o</sup>C under vacuum, and packed in an Argon filled glovebox. The DEPTH sequence was used for all materials. The  $\pi/2$  and  $\pi$  pulse widths for proton were 2.5 µs and 5.0 µs, respectively. The recycle delay was 50 ms (T<sub>1</sub> ≈ 9 ms) with an acquisitions time of 3 ms. 1024 scans were accumulated. All <sup>1</sup>H NMR spectra were referenced to 0.0 ppm to the central line of sodium trimethylsilylpropanesulfonate.

#### Synthesis procedure

**Nanoparticulate**  $Eu_xTb_{(1-x)}BTC$  **MOFs:** The MOF NPs were synthesized following a modified literature procedure.<sup>19</sup> In a typical synthesis of mixed LnBTC ( $Eu_{0.5}Tb_{0.5}BTC$ ), 373.4 mg (4.5 mmol) NaOAc were dissolved in 57 ml DMF and 3 ml deionized H<sub>2</sub>O in a 100 ml round bottom flask equipped with a reflux condenser. Next 339.8 mg (750 µmol) Tb(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, 334.6 mg (750 µmol) Eu(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and 321.7 mg (1.5 mmol) H<sub>3</sub>BTC were added and the synthesis mixture was heated to 110 °C and stirred at this temperature for 4 h (300 rpm). After cooling to room temperature, the white solid was isolated by centrifugation, washed with ca. 30 ml DMF and 30 ml absolute ethanol (three times). The white slurry was dried in an oven at 80 °C. Isolated yield: 471.3 mg (1.02 mmol, 68 %).

All  $Eu_xTb_{(1-x)}BTC$  NP samples were prepared following the procedure described above and are denoted accordingly to the experimentally determined molar ratios as:  $Eu_xTb_{(1-x)}BTC$ MOFs [x = 0 to 1].

#### **Results and Discussion**

#### Mixed-metal Eu/Tb BTC MOFs

The PXRD patterns of the as-synthesized LnBTC MOFs with varying ratios of Eu and Tb in the synthesis mixture (Eu<sub>x</sub>Tb<sub>(1-x)</sub>BTC MOFs [x = 0.0 to 1.0]) are very similar and show the characteristic peaks for the parent EuBTC<sup>13</sup> and [TbBTC]·(DMF)(H<sub>2</sub>O<sub>0.5</sub>) (Figure 1a & Figure S1).<sup>24</sup> The high similarity of the patterns confirm that a series of isostructural MOF was obtained. As the materials were obtained as nanoparticular powders (Figure 1e,f), they exhibit rather broad peaks. Thus, small changes in lattice parameters cannot be observed, which might be expected when gradually replacing Eu with Tb. We note that the composition in the Eu<sub>x</sub>Tb<sub>(1-x)</sub>BTC has an impact on the crystal shape: While the pure LnBTCs were obtained as spherical particles, the mixed-LnBTCs are needle-shaped (Figure 1e,f). The characteristic length of the particles is always below 500 nm.

The thermal stability and decomposition behaviour of all materials is very similar as observed by thermogravimetric analysis (TGA) in air. Between room temperature and 275 °C desorption of remaining ethanol, water and/or DMF occur, while network decomposition only starts above 350 °C. In line with the expected values for the two pure phases, the relative mass loss above 350 °C changes from approx. 49 % in case of EuBTC to approx. 47 % in case of TbBTC. As final products of the decomposition Eu<sub>2</sub>O<sub>3</sub> and Tb<sub>4</sub>O<sub>7</sub> are obtained.<sup>25</sup> The results from TGA, combined with results from inductively coupled plasma optical emission spectroscopy (ICP OES), are thus indicative for an almost perfect 1:1 stoichiometry between lanthanides and BTC. Indeed, using ICP OES, only traces of sodium (<1 %, Table 1) are detected in all materials. The almost perfect stoichiometry is further evidenced by IR spectroscopy. The vanishing of the characteristic  $v_{as}(COO)$  vibration of H<sub>3</sub>BTC around 1720 cm<sup>-1</sup> in all MOFs of the series highlights that hardly any missing cluster defect is present (Figure 1c). Such a defect would give rise to only partially deprotonated H<sub>3</sub>BTC, which would in turn be characterised by its vibration around 1720 cm<sup>-1</sup>. Likewise, only traces of acetate might be present in this series of samples, as the characteristic CH vibrations around 2990 and 2930 cm<sup>-1</sup> are barely visible. The apparent surface area of the series was evaluated using nitrogen as probe molecule. After activation at 250 °C in vacuum for at least 4 hours, all MOFs show type I isotherms. The apparent surface areas vary between 410 and 630 m<sup>2</sup>/g for EuBTC and Eu<sub>0.48</sub>Tb<sub>0.52</sub>BTC, respectively (Table 1). All MOFs show pore volume of approx. 0.2 to 0.3  $\text{cm}^3/\text{g}$  (Table 1). The apparent surface area of the MOFs are in line with literature reports on Tb and Eu MOFs,<sup>20,24</sup>, but slightly lower as compared to their Ho, Tm, Lu and Dy counterparts.<sup>26</sup> To the best of our knowledge no apparent surface areas have been reported for similar mixed LnBTCs, albeit widely used. 12, 19, 22, 23



Figure 1. a) PXRD patterns of as-synthesized  $Eu_xTb_{(1-x)}BTC$  MOFs [x = 0.0 to 1]. Bragg marker for [EuBTC (H<sub>2</sub>O)]·(H<sub>2</sub>O)<sub>1.5</sub> (red, CCDC 617492<sup>13</sup>) and [TbBTC]·(DMF)(H<sub>2</sub>O)<sub>0.5</sub> (green<sup>24</sup>). b) TGA recorded under synthetic air (2K/min heating rate), c) IR spectra of  $Eu_xTb_{(1-x)}BTC$  MOFs (same color code as in a) together with the IR spectrum of H<sub>3</sub>BTC (dark grey) and NaOAc (light grey) and d) N<sub>2</sub> physisorption isotherms recorded at 77 K (same color code as in a), closed symbols denote the adsorption, open symbols indicate the desorption branch). Exemplary SEM images of e) TbBTC and f)  $Eu_{0.04}Tb_{0.96}BTC$  highlighting the characteristic shape of the particles. Scale bar 1 µm.

Table 1. Overview of metal content ( $\omega_i$ ), apparent surface areas ( $S_{BET}$ ) and total pore volumes ( $V_p$ ) in the series of LnBTCs.

material	$\omega_{\rm Eu}{}^{\rm a}$ / wt-%	$\omega_{\mathrm{Tb}}^{b}$ / wt-%	$\omega_{\rm Na}{}^{\rm a}$ / wt-%	$S_{\rm BET}^{\rm c} / {\rm m}^2/{\rm g}$	$V_{\rm p}^{\rm d}$ / cm <sup>3</sup> /g
EuBTC	$31.9 \pm 0.2$		$0.49 \pm 0.01$	410	0.24
Eu <sub>0.70</sub> Tb <sub>0.30</sub> BTC	$23.7\pm0.1$	10.5	$0.62 \pm 0.01$	450	0.32
	160.01	10.0		(20)	0.01
Eu <sub>0.48</sub> Tb <sub>0.52</sub> BTC	$16.2 \pm 0.1$	18.0	$0.24 \pm 0.01$	630	0.31
Eu <sub>0.24</sub> Tb <sub>0.76</sub> BTC	$7.98 \pm 0.16$	27.0	$0.17 \pm 0.01$	510	0.32

Eu0.04Tb0.96BTC	$1.40 \pm 0.02$	32.9	$0.52 \pm 0.01$	500	0.28
Eu0.02Tb0.98BTC	$0.58 \pm 0.01$	34.3	$0.20 \pm 0.01$	510	0.22
TbBTC		41.0	$0.15 \pm 0.01$	510	0.20

<sup>a</sup> determined by ICP OES analysis; <sup>b</sup> calculated from TGA, assuming the formation of Eu<sub>2</sub>O<sub>3</sub>, Tb<sub>4</sub>O<sub>7</sub> and Na<sub>2</sub>O as decomposition products<sup>25</sup>; <sup>c</sup> determined from N<sub>2</sub> physisorption experiments at 77 k, at 0.05 <  $p/p_0$ ; <sup>d</sup> determined from N<sub>2</sub> physisorption experiments at 77 K, at 0.99  $p/p_0$ 

## <sup>1</sup>H solid state NMR spectroscopy

Recently, Blahut *et al.* demonstrated the use of magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy as a powerful toolbox to obtain insight into fine details of the structure of paramagnetic MOFs.<sup>27</sup> Here we recorded <sup>1</sup>H MAS NMR spectra at fast MAS of 30 kHz on the single lanthanide MOFs, EuBTC and TbBTC, and the mixed-metal phases Eu<sub>x</sub>Tb<sub>(1-x)</sub>BTC. Both single-metal MOFs are paramagnetic, however, Eu<sup>3+</sup> in the ground state of the [Xe] 4f<sup>6</sup> configuration often exhibits an angular momentum of 0, leading to no paramagnetic shift anisotropy, contact shift or pseudo-contact shift, whereas Tb<sup>3+</sup> exhibits sizable values for these paramagnet-induced interactions.<sup>28</sup> This is also reflected by the different aspects of the <sup>1</sup>H MAS NMR spectra: The <sup>1</sup>H MAS NMR spectrum of pure EuBTC shows three resonances and well-defined spinning sidebands. We tentatively assign the resonance at approx. 1.6 ppm to water molecules coordinated to defects in the MOF structure and the resonances at ca. 8 and -4 ppm to the two different proton positions of the aromatic protons of BTC present in the asymmetric unit of EuBTC.<sup>13</sup> For comparison, in the <sup>1</sup>H NMR spectrum of paramagnetic Cu<sub>3</sub>BTC<sub>2</sub> only one resonance for aromatic protons has been observed,<sup>29,30</sup> since the asymmetric unit only contains one proton position.<sup>31</sup>

The <sup>1</sup>H MAS NMR spectrum of pure TbBTC is contains three resonances. The resonance of the water molecules is shifted to 4.7 ppm. The resonances of the aromatic protons are shifted to ca. 70 ppm and -62 ppm. These extreme values of 1H chemical shifts are caused by significant paramagnetic contributions, including shift anisotropy, contact shifts or pseudo-

contact shifts induced by  $Tb^{3+}$ . Interestingly, in the <sup>1</sup>H MAS NMR spectra of the series of mixed metal  $Eu_xTb_{(1-x)}BTC$  MOFs, with increasing  $Tb^{3+}$  content, we observe an almost continuous evolution of the chemical shifts of the two aromatic proton positions from on pure phase to the other. Thus each proton in the mixed metal  $Eu_xTb_{(1-x)}BTC$  MOFs is influenced by paramagnetic effects of both metal ions, experimentally confirming that the two cations a homogeneously distributed in the MOFs, without the formation of large Eu- or Tb-rich domains or even co-crystallization of phase-pure MOFs. This unprecedented insight into cation distribution is crucial for the understanding of other material properties such as photo physics (vide infra).



Figure 2. <sup>1</sup>H MAS NMR spectra of  $Eu_xTb_{(1-x)}BTC$  recorded at 500 MHz. Asterisks denote spinning sidebands.

### Luminescent properties of Eu<sub>x</sub>Tb<sub>(1-x)</sub>BTC MOFs

The photoluminescence (PL) spectra of the samples were measured in the solid state and dispersed in ethanol (EtOH) and acetonitrile (ACN). In the solid state, upon excitation at  $\lambda_{ex} = 254$  nm, the pure TbBTC shows the characteristic emissions centered at approx. 489 ( ${}^{5}D_{4} \rightarrow {}^{7}F_{6}$ ), 545 ( ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ ), 586 ( ${}^{5}D_{4} \rightarrow {}^{7}F_{4}$ ) and 622 nm ( ${}^{5}D_{4} \rightarrow {}^{7}F_{3}$ ). With decreasing Tb content in the Eu<sub>x</sub>Tb<sub>(1-x)</sub>BTC series, the intensity of those lines decreases, while the intensity of the lines characteristic for Eu centered emissions at 595 ( ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ ), 616 ( ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ ), 653 ( ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ )

 ${}^{7}F_{3}$ ) and 695 nm ( ${}^{5}D_{0} \rightarrow {}^{7}F_{4}$ ),<sup>32</sup> increases for low Eu ratios and decrease for higher Eu ratios. We note that, as soon as Eu is added, the Tb emission decreases and vanishes almost completely from an Eu content of 25 % onwards. Such a decrease of the Tb emission intensity upon doping the framework with Eu has also been observed in e.g. series of  $[Tb_{2x}Eu_{2\cdot2x}(bdc)_{3}(H_{2}O)_{4}]_{\infty}$  or  $Eu_{x}Tb_{1-x}DMBDC$  MOFs,<sup>33,34</sup> and has been attributed to an efficient, most likely Förster type, energy transfer from Tb to Eu.<sup>35–37</sup> The decrease in Eu emission with increasing Eu content might be attributed to concertation quenching in form of energy migration from Eu<sup>3+</sup> to a nonradiative recombination site or by cross relaxation with other (excited) Eu sites.<sup>34</sup> As the excitation mainly occurs on the ligand, the energy transfer thus also involves excited states of the linker. The excited states energy of the BTC linker is higher than the  ${}^{5}D_{4}$  (Tb) and  ${}^{5}D_{1}$  (Eu) energetic levels. We supposed that similarly to literature reports, energy transfer occurs via intersystem crossing from linker based triplet states to the  ${}^{5}D_{1}$  level, internal conversion into  ${}^{4}D_{0}$  energy level occurred, followed by emission into  ${}^{7}F_{4}$  levels.<sup>38</sup>



Figure 3. a) PL spectra of  $Eu_x Tb_{(1-x)}BTC$  MOFs [x = 0.0 to 1.0] in the solid state ( $\lambda_{ex}$ : 254 nm), b) corresponding quenching ratio of the Tb emission at 489 nm (purple) and 543 nm (dark gray). Comparison of solid-state photoluminescence spectra with PL spectra obtained for the MOF dispersions in ethanol and acetonitrile of (c) EuBTC and (d) TbBTC ( $\lambda_{ex}$ : 300 nm).

The emission spectra of dispersions of the pure TbBTC MOF in ethanol or in acetonitrile are very similar to the PL spectra in the solid state (Figure 3). The absence of any significant solvatochromic behavior in TbBTC is corroborated by reports on molecular Tb<sup>3+</sup> complexes.<sup>39-</sup> <sup>41</sup> In case of EuBTC significant solvatochromic effects are observed, in particular on the  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  ( $\Delta J = 2$  manifold) and  ${}^{5}D_{0} \rightarrow {}^{7}F_{4}$  ( $\Delta J = 4$  manifold) transition. When dispersed in ethanol, the emission spectrum of EuBTC is characterized by a slight shift of the emission wavelength and a more pronounced stark splitting of the  $\Delta J = 2$  manifold: instead of a broad band, three well resolved bands can be distinguished. When replacing ethanol with acetonitrile, the stark splitting of the <sup>7</sup>F<sub>2</sub> manifold is less pronounced, with an almost unaffected position of the highest energy transition. These changes in stark splitting of the manifold have been correlated to the change of the solvent's polarity. With increasing solvent polarity the difference between lower energy transitions decreases, causing a less pronounced ligand field splitting of the <sup>7</sup>F<sub>J</sub> levels.<sup>42</sup> Likewise, also more pronounced stark splitting are observed for the  $\Delta J = 1$  and  $\Delta J = 2$  manifolds. For the  $\Delta J = 4$  manifold, the stark splitting is almost invisible when EuBTC is dispersed in acetonitrile, resulting in an increase in the relative intensities of the transition as compared to the PL spectra recorded in ethanol and in the dry solid state. Overall the solvatochromic behavior of the Eu<sup>3+</sup> luminescent centers follows the same trends observed for organometallic Eu complexes.<sup>42</sup> The observed changes are thus most likely caused by a change in the solvents polarity,<sup>42</sup> but contributions from solvent coordination to open metal sites and/or H-bonding cannot be ruled out. The diffrent solvatochromic behaviors of Eu and Tb luminescent centers in EuBTC and TbBTC are also observed in the Eu<sub>x</sub>Tb<sub>(1-x)</sub>BTC series (Figure S2), opening the possibility for dual ratiometric temperature and solvent sensing (vide infra).

Temperature-dependent luminescence spectra were recorded for Eu<sub>0.04</sub>Tb<sub>0.96</sub>BTC and Eu<sub>0.02</sub>Tb<sub>0.98</sub>BTC in the temperature range from 200 to 330 K in the solid state. The terbiumbased emission, e.g. at 488 nm and 542 nm, decreases linearly with increasing temperature. We note that there seems to be a discontinuity between 280 and 300 K. However, for the Eu-based emission, the temperature dependency is more complex. Between 200 and 270 K, the emission decreases linearly with increasing temperature, while above 270 K it increases again. Between 280 and 300 K also for the Eu-based emissions, there is a discontinuity observed. This discontinuity of the emission is however not correlated to a phase transition of the MOFs as evidenced by dynamic scanning calorimetry (Figure S3).

In the range from 200 to 270 K, the decrease in emission is stronger for Tb than for Eu-based emission, for both materials and in line with results on single lanthanide  $Ln_2(Hpcpa)_3(H_2O)_5 \cdot H_2O$  ( $H_3pcpa = N$ -(4-carboxyphenyl)oxamic acid).<sup>32</sup> For EuBTC doped with CsPbBr<sub>3</sub> quantum dots,<sup>21</sup> as well as Eu<sub>0.37</sub>Tb<sub>0.63</sub>BTC,<sup>12</sup> an increase in emission with increasing temperature above 293 K has been reported. In contrast for a series of Eu<sub>x</sub>Tb<sub>(1-x)</sub>-DMBDC (x = 0.0011, 0.0046, 0.0069; DMBDC = 2,5-dimethoxy-1,4-benzenedicarboxylate) a different behaviour has been reported.<sup>36</sup> While the Tb emission still decreases with increasing temperature, the Eu emission increases with increasing temperature in the range from 10 to 300 K. Interestingly for pure Eu-DMBDC and pure Tb-DMBDC, a decrease of the emission with increasing temperature has been reported. The inversion of the temperature dependency of the Eu emission when doped into the Tb-DMBDC matrix has been explained by an efficient energy transfer from Tb to Eu.



Figure 4. Temperature dependent luminescence spectra recoded between 200 and 330 K after excitation at 370 nm of a) Eu<sub>0.04</sub>Tb<sub>0.96</sub>BTC and c) Eu<sub>0.02</sub>Tb<sub>0.98</sub>BTC. Corresponding evolution of the luminescence with temperature, expressed as area at a given temperature divided by the area at 200 K, for b) Eu<sub>0.04</sub>Tb<sub>0.96</sub>BTC and d) Eu<sub>0.02</sub>Tb<sub>0.98</sub>BTC. Gray circles highlight the region of discontinuity in the temperature dependency.

The efficiency of this energy transfer increases with temperature and with decreasing amount of Eu.<sup>36</sup> The difference to the observed profile of Eu<sub>0.04</sub>Tb<sub>0.96</sub>BTC as well as Eu<sub>0.02</sub>Tb<sub>0.98</sub>BTC might be the higher amount of Eu used in our study, making the energy transfer per Eu atom less efficient as compared to the Eu<sub>0.0069</sub>Tb<sub>0.9931</sub>-DMBDC system, in particular at low temperatures. As the efficiency of the energy transfer will most likely also increase with temperature in the Eu<sub>0.04</sub>Tb<sub>0.96</sub>BTC and Eu<sub>0.02</sub>Tb<sub>0.98</sub>BTC systems, this might explain the increase in the Eu emission above 270 K. In case of Eu<sub>0.02</sub>Tb<sub>0.98</sub>BTC, the lifetime of the Eu <sup>5</sup>D<sub>0</sub>

→  ${}^{7}F_{2}$  transition is almost constant in the entire temperature range investigated, while the lifetime of the Tb  ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$  transition decreases with increasing temperature (Figure 5). The long rise time of the decay line of the Eu  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transition might also hint to an energy transfer between the two luminescent centers.



Figure 5. PL decay curves as a function of temperature recorded on (a) the Eu  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transition and (b) the Tb  ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$  transition.

For the application as ratiometric temperature sensor we used the ratio of the integrated area of Tb emission ( ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$  or  ${}^{5}D_{4} \rightarrow {}^{7}F_{6}$ ) with respect to the integrated area of the europium  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  emission. Caused by the discontinuity in the emission profiles between 270 and 280 K, sets of two different linear calibration curves were obtained for each material. Independently of the MOFs composition, the ratios  $\frac{I_{\text{Tb}(5}D_{4} \rightarrow {}^{7}F_{5})}{I_{\text{Eu}(5}D_{0} \rightarrow {}^{7}F_{2})}$  and  $\frac{I_{\text{Tb}(5}D_{4} \rightarrow {}^{7}F_{6})}{I_{\text{Eu}(5}D_{0} \rightarrow {}^{7}F_{2})}$  show a stronger temperature dependency above 280 K.



Figure 6. Evolution of temperature as a function of the luminescence ratios, expressed as area at a given temperature for the terbium emission (purple  ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ , gray  ${}^{5}D_{4} \rightarrow {}^{7}F_{6}$ ) divided by the area of the europium emission ( ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ ), for a) Eu<sub>0.02</sub>Tb<sub>0.98</sub>BTC and b) Eu<sub>0.04</sub>Tb<sub>0.96</sub>BTC.

Interestingly when Eu<sub>0.02</sub>Tb<sub>0.98</sub>BTC is used as temperature probe dispersed in ethanol or acetonitrile (Figure 7), no discontinuity of the emission is observed in the temperature range from 250 to 330 K. Thus the ratios of terbium over europium emission  $\left(\frac{I_{\text{Tb}}(^{5}\text{D}_{4} \rightarrow ^{7}\text{F}_{5})}{I_{\text{Eu}}(^{5}\text{D}_{4} \rightarrow ^{7}\text{F}_{2})}\right)$  and  $I_{\text{Tb}}(^{5}\text{D}_{4} \rightarrow ^{7}\text{F}_{2})$  the ratio of terbium over europium emission ( $I_{\text{Eu}}(^{5}\text{D}_{0} \rightarrow ^{7}\text{F}_{2})$ )

 $\frac{I_{\text{Tb}}(5_{D_4} \rightarrow 7_{F_6})}{I_{\text{Eu}}(5_{D_0} \rightarrow 7_{F_2})}$  linearly decreases over the whole temperature range. As for the pure MOFs (Figure 3c,d), solvation with either acetonitrile or ethanol tremendously affects the emission profile also for Eu<sub>0.02</sub>Tb<sub>0.98</sub>BTC. When dispersed in acetonitrile, the europium  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  emission is stronger than the most intense terbium emission ( ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ ), indicative for a better energy transfer from terbium to europium as compared to the dispersion in ethanol. Thus by comparing the two calibration factors it is not only possible to determine the temperature but to discern different solvents as shown here for ethanol and acetonitrile.



Figure 7. Temperature dependent luminescence spectra recoded between 253 and 333 K after excitation at 254 nm of  $Eu_{0.02}Tb_{0.98}BTC$  dispersed in a) ethanol and c) acetonitrile. Corresponding evolution of the luminescence ratio with temperature, expressed as area at a given temperature for the terbium emission (purple  ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ , gray  ${}^{5}D_{4} \rightarrow {}^{7}F_{6}$ ) divided by the area of the europium emission ( ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ ), for dispersion in b) ethanol and d) acetonitrile.

# Conclusions

Using the acetate mediated synthesis protocol of LnBTCs, we obtained a series of  $Eu_xTb_{(1-x)}BTC$  MOFs, in which the ratio of the two lanthanides is controlled by the synthesis gel composition. Using <sup>1</sup>H MAS NMR spectroscopy, we demonstrated the homogeneous incorporation of both cations in the series of mixed metal  $Eu_xTb_{(1-x)}BTC$  MOFs. The <sup>1</sup>H NMR chemical shifts of the two crystallographically different protons change continuously in the

series from on pure LnBTC MOF to the other, indicating the formation of a single crystalline phase with homogeneous distribution of the two different metals. The precise control of lanthanide stoichiometry and distribution allows to control the luminescent properties of the final material. While for Eu loadings above 25 mol% the Tb emission is completely quenched, in Eu<sub>0.04</sub>Tb<sub>0.96</sub>BTC still 20% of the Tb emission intensity of the parent TbBTC remains, sufficient to be used as a rational temperature sensor. Eu<sub>0.04</sub>Tb<sub>0.96</sub>BTC and Eu<sub>0.02</sub>Tb<sub>0.98</sub>BTC allow for rational temperature sensing in the range between 200 and 270 K and above 300 K. Interestingly, the emission profiles of Tb centres are hardly affected when the material is dispersed in different solvents, while for Eu centres the emission wavelengths of the transitions as well as the intensity ratios for the different transitions change in the presence of ethanol and acetonitrile. Therefore, the solvation of the MOFs should be considered when using them as rational temperature sensors in the presences of solvents or vapours. This solvation dependency of the lanthanide emission can be rationalised and taken into account in such sensors, to determine temperature and discern between different solvents present as demonstrated here for acetonitrile and ethanol as model compounds.

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