Heterometallic Europium(III)–Lutetium(III) Terephthalates as Bright Luminescent Antenna MOFs

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Abstract: A new series of luminescent heterometallic europium(III)–lutetium(III) terephthalate metal–organic frameworks, namely \((\text{Eu}_x\text{Lu}_{1-x})_2\text{bdc}_3\cdot n\text{H}_2\text{O}\), was synthesized using a direct reaction in a water solution. At the \(\text{Eu}^{3+}\) concentration of 1–40 at %, the MOFs were formed as a binary mixture of the \((\text{Eu}_x\text{Lu}_{1-x})_2\text{bdc}_3\) and \((\text{Eu}_x\text{Lu}_{1-x})_2\text{bdc}_3\cdot 4\text{H}_2\text{O}\) crystalline phases, where the \(\text{Ln}_2\text{bdc}_3\cdot 4\text{H}_2\text{O}\) crystalline phase was enriched by europium(III) ions. At an \(\text{Eu}^{3+}\) concentration of more than 40 at %, only one crystalline phase was formed: \((\text{Eu}_x\text{Lu}_{1-x})_2\text{bdc}_3\cdot 4\text{H}_2\text{O}\). All MOFs containing \(\text{Eu}^{3+}\) exhibited sensitization of bright \(\text{Eu}^{3+}\)-centered luminescence upon the 280 nm excitation into a \(1\pi\pi^*\) excited state of the terephthalate ion. The fine structure of the emission spectra of \(\text{Eu}^{3+}\) was significantly larger for \(\text{Eu}-\text{Lu}\) terephthalates containing a low concentration of \(\text{Eu}^{3+}\) due to the absence of \(\text{Eu}-\text{Eu}\) energy migration and the presence of the \(\text{Ln}_2\text{bdc}_3\) crystalline phase with a significantly smaller nonradiative decay rate compared to the \(\text{Ln}_2\text{bdc}_3\cdot 4\text{H}_2\text{O}\).

Keywords: metal–organic framework; luminescence; rare earth; europium; lutetium; phase transition

1. Introduction

In recent decades, rare-earth-element metal–organic frameworks (REE-MOFs) were actively designed and synthesized due to their unique luminescence properties. They are unique platforms for fabricating advanced luminescent materials, which are widely used in various fields of science and technology [1–4]. The position of the lanthanide ionic luminescence bands strongly depends only on the lanthanide ion, which allows the construction of REE-MOFs with the desired optical properties [5]. Taking this fact into account and considering the high stability, low solubility and toxicity, and highly effective charge transport of Ln-MOFs, they are prospective materials for OLEDs [6,7], luminescent thermometers [8,9], and imaging [10–13]. Variations in organic linkers in MOFs allow synthetic chemists to form structures with different porosities, large surface areas, and high structural flexibility [14–16], which allows the use of REE-MOFs as highly selective sensors on organic and inorganic materials [17–25]. Typical linkers in REE-MOFs are organic carboxylates due to the simple synthesis of REE-MOFs in undemanding conditions and the unlimited possibilities in MOF design [26,27].

Lanthanide ions possess characteristic luminescence; however, direct UV excitation of them is inefficient because they have very small light absorption coefficients: 4f-4f transitions are forbidden by selection rules. This issue can be resolved using the energy transfer from the excited linker to the lanthanide ion (antenna effect) [28,29]. Aromatic organic molecules such as 1,4-benzenedicarboxylate (bdc) are widely used as antenna linkers due to their effective UV absorbance and pronounced antenna effect [30,31]. Usually,
the energy transfer takes place from the lower-level triplet electronic state (T₁) of the linker molecule but not from the lowest excited singlet state (S₁). In some cases, the heavy lanthanides increase the rate of S₁-T₁ intersystem crossing [32–35]. The high concentration of luminescent lanthanide ion in homometallic REE-MOFs could result in concentration quenching through Ln-Ln energy migration and, therefore, the drop in luminescence quantum yield (PLQY) [36]. Utochnikova et al. proposed a solution to this problem by doping of a luminescent europium(III) terephthalate with nonluminescent Gd³⁺ ions, which not only diluted the luminescent Tb³⁺ ions, but also increased the probability of intersystem crossing, which increased the PLQY. It was found that Eu-Gd and Eu-Y heterometallic terephthalates were formed in the same crystalline phases. In the current work, we studied a series of luminescent heterometallic europium(III)–lutetium(III) terephthalates MOFs and observed that the substitution of a large amount of Eu(III) for Lu(III) resulted in a crystalline phase change as well as a significant rise in the PLQY.

2. Results and Discussion

2.1. XRD Results and Analysis

The X-ray powder diffraction (XRD) patterns (Figure 1a) were measured for the range of heterometallic europium(III)–lutetium(III) terephthalates (Eu₃Lu₁₋ₓ)bdc₃·nH₂O; bdc = 1,4-benzenedicarboxylate) with a Eu³⁺ concentration from 0 to 100 at %. An analysis of the XRD patterns demonstrated that in a range of Eu³⁺ concentration of 6 to 100 at %, the samples were isostructural to the Ln₂bdc₃·4H₂O (Ln = Ce–Yb) [37]. This structure, which is common for the rare-earth terephthalates from Ce to Yb [38], was a three-dimensional metal–organic framework (MOF) in which octacoordinated lanthanide ions were bound to the two water molecules and six terephthalate ions through the oxygen atoms (Figure 1b). The analysis of XRD patterns of Eu-Lu terephthalates with 0–2 at % of Eu³⁺ showed that the samples are isostructural to Er₂bdc₃ [38], which is a 3D MOF in which heptacoordinated lanthanide ions are bound to the seven oxygen atoms from the terephthalate ions (Figure 1c). At a Eu³⁺ concentration in the range of 3–5 at %, both the Ln₂bdc₃·4H₂O and Ln₂bdc₃ crystalline phases were observed. The XRD peaks for heterometallic europium(III)–lutetium(III) terephthalates in Eu³⁺ concentration ranged from 6 to 100 at % and were slightly shifted relative to the XRD peaks measured for Ln₂bdc₃·4H₂O reported previously [37]. To compare these Ln₂bdc₃·4H₂O structures, the refinement of unit cell parameters was performed for some samples with a Eu³⁺ concentration between 6 and 100 at % (Table 1) using UnitCell software [39], which retrieved unit cell parameters from diffraction data using a method of least squares from the 2Θ data of the XRD patterns. Calculation errors also are shown in Table 1. We observed that in the range, the unit cell parameters increased. The observed growth of the unit cell parameters of heterometallic europium(III)–lutetium(III) terephthalates was explained by the smaller ionic radius of the octacoordinated Lu³⁺ (0.977 Å) compared with the ionic radius of the Eu³⁺ ion (1.066 Å) [40].

Table 1. Unit cell parameters with calculation errors for (EuₓLu₁₋ₓ)bdc₃·nH₂O refined for Eu₂bdc₃·4H₂O crystalline phase.

| XEu (%) | a, Å | b, Å | c, Å | α | β | γ | V, Å³ |
|--------|------|------|------|---|---|---|------|
| 100    | 6.1904 ± 0.0019 | 9.856 ± 0.003 | 10.251 ± 0.003 | 101.673 ± 0.027 | 90.273 ± 0.028 | 104.796 ± 0.025 | 591.13 ± 0.22 |
| 90     | 6.1862 ± 0.0019 | 9.845 ± 0.003 | 10.236 ± 0.003 | 101.583 ± 0.027 | 90.300 ± 0.028 | 104.727 ± 0.025 | 589.63 ± 0.22 |
| 60     | 6.1727 ± 0.0018 | 9.815 ± 0.003 | 10.206 ± 0.003 | 101.553 ± 0.027 | 90.418 ± 0.028 | 104.657 ± 0.025 | 585.00 ± 0.22 |
| 40     | 6.1635 ± 0.0018 | 9.783 ± 0.003 | 10.179 ± 0.003 | 101.497 ± 0.027 | 90.472 ± 0.028 | 104.651 ± 0.025 | 580.75 ± 0.22 |
| 20     | 6.1405 ± 0.0018 | 9.738 ± 0.003 | 10.145 ± 0.003 | 101.570 ± 0.027 | 90.562 ± 0.028 | 104.617 ± 0.025 | 573.90 ± 0.21 |
Table 1. Cont.

| XEu (%) | a, Å | b, Å | c, Å | α | β | γ | V, Å³ |
|---------|------|------|------|----|----|----|-------|
| 10      | 6.1411 ± 0.0018 | 9.7178 ± 0.0003 | 10.1334 ± 0.0026 | 90.461 ± 0.028 | 104.590 ± 0.025 | 572.13 ± 0.21 |
| 6       | 6.1313 ± 0.0018 | 9.714 ± 0.0003 | 10.130 ± 0.0026 | 90.474 ± 0.027 | 104.608 ± 0.025 | 570.784 ± 0.21 |

Figure 1. (a) The XRD patterns of (EuₓLu₁₋ₓ)₂bdc₃·nH₂O in heterometallic europium(III)–lutetium(III) terephthalate powders from 0% Eu³⁺ to 100% Eu³⁺ and the simulated XRD pattern of Er₂bdc₃ and Eu₂bdc₃·4H₂O single-crystals structure taken from refs. [37,38]. (b,c) The generated crystal structures of Eu₂bdc₃·4H₂O and Er₂bdc₃, respectively.

2.2. Thermogravimetric Analysis (TGA)

The thermogravimetric analysis (TGA) was carried out for the selected heterometallic europium(III)–lutetium(III) terephthalates in a temperature range of 25–300 °C (Figure 2a). The mass loss was observed at 120–180 °C for all measured samples. As previously reported [38], the mass loss in this temperature range can be assigned to the dehydration of the compounds resulting in the formation of Ln₂bdc₃. An analysis of the TGA curves allowed us to calculate the average numbers of water molecules in the heterometallic europium(III)–lutetium(III) terephthalates (EuₓLu₁₋ₓ)₂bdc₃·nH₂O). We observed that this number increased with the increase in the Eu³⁺ concentration (Figure 2b). An analysis of the XRD patterns demonstrated the presence of two crystalline phases: Ln₂bdc₃·4H₂O and Ln₂bdc₃. Therefore, we could estimate the molar fraction of each coexisting crystalline phase (Figure 2c). The molar fraction of Ln₂bdc₃·4H₂O increased along with the Eu³⁺ concentration in a range between 0 and 40 at %. In the Eu³⁺ concentration range of 40–100%, only Ln₂bdc₃·4H₂O was present.
2.3. Luminescent Properties

The terephthalate ion is a typical linker used in luminescent antenna MOFs [41] due to its intensive UV absorbance [42] followed by efficient energy transfer to the luminescent lanthanide ion. The excitation of (Eu$_{x}$Lu$_{1-x}$)$_{2}$bdc$_{3}$·nH$_{2}$O ($\lambda_{\text{ex.}}$ = 280 nm) resulted in emission in the visible range corresponding to 5D$_{0}$-7F$_{J}$ ($J$ = 0–5) transitions of the Eu$^{3+}$ ion [5] (Figures 3 and 4). Upon UV excitation, the terephthalate ion was promoted into the S$_{1}(^{3}\pi\pi^{*})$ state followed by the fast internal conversion to S$_{1}(^{1}\pi\pi^{*})$. Due to the heavy atom effect, the S$_{1}$ state efficiently moved to the T$_{1}(^{3}\pi\pi^{*})$ triplet electronic excited state [34] via intersystem crossing. The T$_{1}$ state of the terephthalate ion [34] ($\approx$ 20,000 cm$^{-1}$) had a higher energy than the 5D$_{1}$ energy level of the Eu$^{3+}$ ion [5] ($\approx$ 19,000 cm$^{-1}$) and a significantly lower energy than that of the lower excited state of the Lu$^{3+}$ ion [43] (80,000 cm$^{-1}$). Therefore, an efficient energy transfer from the T$_{1}$ triplet electronic excited state of the terephthalate ion to the 5D$_{1}$ energy level of the Eu$^{3+}$ ion occurred. The 5D$_{1}$ level of the Eu$^{3+}$ ion then underwent an internal conversion into the 5D$_{0}$ energy level followed by the emission into the 7F$_{J}$ ($J$ = 0–4) lower-lying levels.

We observed that the fine structure of the Eu$^{3+}$ emission spectra significantly depended on the Eu$^{3+}$ concentration in the (Eu$_{x}$Lu$_{1-x}$)$_{2}$bdc$_{3}$·nH$_{2}$O (Figure 4). At Eu$^{3+}$ ion concentrations of more than 6 at %, in which the Ln$_{2}$bdc$_{3}$·4H$_{2}$O phase dominated, the emission spectra were similar to that of Eu$_{2}$bdc$_{3}$·4H$_{2}$O [31] and consisted of narrow bands corresponding to 5D$_{0}$-7F$_{J}$ ($J$ = 0–4) transitions of Eu$^{3+}$: 5D$_{0}$-7F$_{0}$ (577.6 nm), 5D$_{0}$-7F$_{1}$ (587.9 and 591.5 nm), 5D$_{0}$-7F$_{2}$ (614.0 nm), 5D$_{0}$-7F$_{3}$ (649.0 nm), and 5D$_{0}$-7F$_{4}$ (697.0 nm) (Figure 3). At low Eu$^{3+}$ concentrations (2 and 4 at % Eu$^{3+}$), in which the Ln$_{2}$bdc$_{3}$ phase dominated, the fine structure of the emission spectra was significantly different. The emission spectra contained 5D$_{0}$-7F$_{0}$ (577.2 nm and 577.6 nm), 5D$_{0}$-7F$_{1}$ (585.9, 588.4, and 595.6 nm), 5D$_{0}$-7F$_{2}$ (616.6, 610.2, 616.6, 619.4 (shoulder), and 621.8 nm), 5D$_{0}$-7F$_{3}$ (649.0 nm), and 5D$_{0}$-7F$_{4}$ (700.0 nm) Eu$^{3+}$ narrow emission bands.
Figure 3. The normalized emission spectra of (Eu$_x$Lu$_{1-x}$)$_2$bdc$_3$·nH$_2$O at selected Eu$^{3+}$ concentrations (given in legend) upon 280 nm excitation.

Figure 4. Fine structure of lines in emission spectra of heterometallic europium(III)–lutetium(III) terephthalates normalized at maximum point for (a) $^5$D$_0$–$^7$F$_0$, (b) $^5$D$_0$–$^7$F$_1$, and (c) $^5$D$_0$–$^7$F$_2$ transitions.

$^5$D$_0$–$^7$F$_0$ transition is strictly forbidden by the Judd–Ofelt theory; one can observe this transition only for europium(III) ions in coordination sites with C$_n$, C$_{nv}$, and C$_s$ symmetry. For all measured samples, $^5$D$_0$–$^7$F$_0$ transitions were observed. The analysis of the fine structure of this transition allowed us to determine the number of Eu$^{3+}$ coordination sites because the $^7$F$_0$ level was not degenerate and did not split in the crystal field, hence $^5$D$_0$–$^7$F$_0$ could present in the emission spectrum as a single line for one type of Eu$^{3+}$ coordination. The fine structure of the (Eu$_x$Lu$_{1-x}$)$_2$bdc$_3$·nH$_2$O emission bands $^5$D$_0$–$^7$F$_0$ is shown in Figure 4a. In the emission spectra of Eu-Lu terephthalates with a Eu$^{3+}$ concentration of 6–100 at %, a single line was observed in the 570–585 nm range ($^5$D$_0$–$^7$F$_0$) with a maximum at 577.6 nm, which indicated that Eu$^{3+}$ ions existed in the single-crystal-phase isostructural Ln$_2$bdc$_3$·4H$_2$O. Meanwhile, by using a TGA, we estimated the molar fractions of Ln$_2$bdc$_3$·4H$_2$O and Ln$_2$bdc$_3$ as equal to 60 and 40%, respectively. Therefore, the single $^5$D$_0$–$^7$F$_0$ emission band (6–100 at % Eu$^{3+}$) can be explained by uneven ion distribution.
between the two phases: the Ln$_2$bdc$_3$·4H$_2$O crystalline phase was enriched by Eu$^{3+}$ ions. In the Eu-Lu terephthalates with 2–4 at % Eu$^{3+}$, two emission bands corresponding to the $^5$D$_0$→$^7$F$_1$ transition were observed to peak at 577.2 and 577.6 nm, indicating the two different coordination sites of the Eu$^{3+}$ ion. Therefore, in the terephthalates containing 2–4 at % Eu$^{3+}$, europium(III) ions were distributed between two phases, namely Ln$_2$bdc$_3$·4H$_2$O and Ln$_2$bdc$_3$, which was consistent with the TGA and XRD data.

The fine structure of the $^5$D$_0$→$^7$F$_1$ emission bands and their relative intensities were very sensitive to the Eu$^{3+}$ ions’ local symmetry. The degeneracy of each spin–orbit level was 2$J$+1 [5]. Hence, the maximum amount of crystal-field transitions of the $^5$D$_0$→$^7$F$_2$ transitions were 3 and 5, respectively. According to previous studies, lanthanide(III) ions had pseudo-C$_4$ symmetry in Ln$_2$bdc$_3$·4H$_2$O (Ln = Tb, Eu) [38]. For Eu$_2$bdc$_3$·4H$_2$O (100 at % Eu$^{3+}$), the $^5$D$_0$→$^7$F$_1$ transition split into two crystal field transitions (587.9 and 591.6 nm), and the $^5$D$_0$→$^7$F$_2$ transition was presented in the emission spectrum as a single line (614.0 nm). Interestingly, for the Eu-Lu terephthalates containing 6–60 at % Eu$^{3+}$, different splitting patterns of the $^5$D$_0$→$^7$F$_1$ transitions in the crystal field were observed. The $^5$D$_0$→$^7$F$_1$ and $^5$D$_0$→$^7$F$_2$ transition split into three (587.6, 591.0, and 592.8 nm) and two components (608.5 and 614.0 nm), respectively (Figure 4b,c). The difference between the abovementioned emission spectra can be explained by the distortion of the coordination polyhedron due to the appearance of structural defects caused by the addition of Lu$^{3+}$ ions, which have a lower ionic radius than europium(III) ions (lanthanide contraction). This resulted in the lowering of the local symmetry of the Eu$^{3+}$ ion and the larger number of crystal-field transitions of Eu-Lu terephthalates compared to the Eu$_2$bdc$_3$·4H$_2$O. The number of $^5$D$_0$→$^7$F$_1$ crystal-field transitions indicated that the Eu$^{3+}$ had symmetry of C$_2$ or lower [44].

In the emission spectra of Ln$_2$bdc$_3$ (2–4 at % Eu$^{3+}$), the $^5$D$_0$→$^7$F$_1$ and $^5$D$_0$→$^7$F$_2$ transitions split into three (585.9, 588.4, and 595.6 nm) and five components (606.6, 610.2, 616.6, 619.4 (shoulder), and 621.8 nm), respectively. In the emission spectra of the Lu-Eu terephthalates containing 2–4 at % Eu$^{3+}$, we observed the presence of (Eu$_x$Lu$_{1-x}$)$_2$bdc$_3$·4H$_2$O emission bands (weak 608.5 and 614.0 nm signals) because the Eu$^{3+}$ ion was distributed between the Ln$_2$bdc$_3$ and Ln$_2$bdc$_3$·4H$_2$O crystalline phases. A careful analysis of the Ln$_2$bdc$_3$ crystalline structure (Figure 1c) allowed us to conclude that the Ln$^{3+}$ ion had C$_1$ local symmetry, which was consistent with the number of crystal-field components of the $^5$D$_0$→$^7$F$_0$, $^5$D$_0$→$^7$F$_1$, and $^5$D$_0$→$^7$F$_2$ transitions (1, 3, and 5, respectively) [44].

The luminescence decay curves of the (Eu$_x$Lu$_{1-x}$)$_2$bdc$_3$·nH$_2$O phosphors monitored at 615 nm ($^5$D$_0$→$^7$F$_2$ transition) are presented in Figure 5 ($\lambda_{ex}$ = 280 nm). At a low Eu$^{3+}$ concentration (2 and 4 at %), the decay curves were fitted by a double exponential function (1), whereas the decay curves of the Eu-Lu terephthalates containing 6–100 at % Eu$^{3+}$ were fitted by a single exponential function (2):

\[
I = I_1e^{-\frac{t}{\tau_1}} + I_2e^{-\frac{t}{\tau_2}}
\]  

(1)  

\[
I = I_1e^{-\frac{t}{\tau}}
\]  

(2)

where $\tau_1$ and $\tau_2$ are the observed $^5$D$_0$ lifetimes (Table 2).

**Table 2.** The lifetimes of excitation state 5D0 of Eu$^{3+}$ in heterometallic europium(III)–lutetium(III) terephthalates at 2, 4, 6, 10, 60, and 100 at % Eu.

| $x_{Eu}$ (%) | $\tau_1$, ms | $\tau_2$, ms | PLQY, % |
|-------------|--------------|--------------|---------|
| 100         | 0.390        |              | 10 ± 1  |
| 60          | 0.435        |              | 11 ± 1  |
| 10          | 0.449        |              | 12 ± 1  |
| 6           | 0.459        |              | 16 ± 1  |
| 4           | 0.392        | 1.602        | 22 ± 1  |
| 2           | 0.367        | 1.878        | 22 ± 1  |
Figure 5. The 615 nm luminescence decay curves of heterometallic europium(III)–lutetium(III) terephthalates at 2, 4, 6, 10, 60, and 100 at % Eu.

The Eu-Lu terephthalates containing 6–100 at % Eu$^{3+}$ had 5D$_0$ lifetimes of 0.390–0.459 ms and luminescence quantum yields of 10–16%. The measured PLQY of the Eu$_2$bd$_3$·4H$_2$O was comparable with the literature data [31,38,45]. The 5D$_0$ lifetime values and the luminescence quantum yields decreased with an increase in the Eu$^{3+}$ concentration due to the energy migration between the Eu$^{3+}$ ions and subsequent quenching by impurities and defects. We demonstrated in this work that Eu$^{3+}$ ions predominantly existed in the Ln$_2$bd$_3$·4H$_2$O phase in the europium(III)–lutetium(III) terephthalates containing 6–100 at % Eu$^{3+}$, in which the presence of a single Eu$^{3+}$ coordination site resulted in a single 5D$_0$ lifetime. Interestingly, the europium(III)–lutetium(III) terephthalates containing 2–4 at % Eu$^{3+}$ were characterized by two 5D$_0$ lifetimes. One emission decay component ($\tau_1 = 0.392–0.367$ ms) was close to the value observed for the europium(III)–lutetium(III) terephthalates containing 6–100 at % Eu$^{3+}$, while another component ($\tau_2 = 1.602–1.878$ ms) was 4–4.8 times larger. In the Eu-Lu terephthalates containing 2–4 at % Eu$^{3+}$, the Eu$^{3+}$ ions were distributed between the Ln$_2$bd$_3$·4H$_2$O and Ln$_2$bd$_3$ crystalline phases. Therefore, $\tau_1$ and $\tau_2$ could be assigned to the Eu$^{3+}$ ions located in the Ln$_2$bd$_3$·4H$_2$O and Ln$_2$bd$_3$, respectively. The water molecules in the Ln$_2$bd$_3$·4H$_2$O structure were coordinated with the Eu$^{3+}$ ion and quenched the Eu$^{3+}$ luminescence due to efficient energy transfer to high-energy O-H stretching vibrational modes of coordinated water molecules [46,47]. In the Ln$_2$bd$_3$ crystalline phase, the Eu$^{3+}$ ion was coordinated only with oxygen atoms of carboxylic groups of terephthalate ions. The efficient quenching of Eu$^{3+}$ ions by water molecules in the Ln$_2$bd$_3$·4H$_2$O structure resulted in a significant decrease in the Eu$^{3+}$ ion 5D$_0$ lifetime compared to anhydrous Ln$_2$bd$_3$. The emission quantum yield of the Eu$^{3+}$ was significantly larger for the Eu-Lu terephthalates doped with a low Eu$^{3+}$ concentration. This observation can be explained by two reasons: the absence of efficient Eu-Eu energy migration and the presence of the Ln$_2$bd$_3$ crystalline phase with a significantly smaller nonradiative decay rate compared to the Ln$_2$bd$_3$·4H$_2$O.

3. Materials and Methods

Lutetium (III) chloride hexahydrate and europium (III) chloride hexahydrate were purchased from Chemcraft (Kaliningrad, Russia). Benzene-1,4-dicarboxylic (terephthalic, H$_2$bd) acid (>98%), sodium hydroxide (>99%), nickel(II) chloride hexahydrate (>99%), and EDTA disodium salt (0.1 M aqueous solution) were purchased from Sigma-Aldrich Pty Ltd. (Germany) and used without additional purification. The 0.2M solutions of EuCl$_3$ and LuCl$_3$ were prepared and standardized using complexometric titration with EDTA. A total of 0.6 mole of sodium hydroxide and 0.3 mole of terephthalic acid were dissolved in distilled water to obtain a 1 L solution of the disodium terephthalate (Na$_2$bd).
The heterometallic europium(III)–lutetium(III) terephthalates were obtained by mixing 1 mL of 0.2 M EuCl$_3$ and LuCl$_3$ aqueous solutions taken in stoichiometric ratios with 2 mL of 0.3 M Na$_2$bdc water solution (Table 3). White precipitates of heterometallic europium(III)–lutetium(III) terephthalates were separated from the reaction mixture using centrifugation (4000 × g) and washed using deionized water 5 times. All samples were dried at 60 °C.

Table 3. The heterometallic europium(III)–lutetium(III) terephthalates’ synthesis conditions.

| $\chi_{\text{Eu}}$, % | V(0.2M EuCl$_3$), mL | V(0.2M LuCl$_3$), mL |
|----------------------|----------------------|----------------------|
| 0                    | 0                    | 1.00                 |
| 1                    | 0.01                 | 0.99                 |
| 2                    | 0.02                 | 0.98                 |
| 3                    | 0.03                 | 0.97                 |
| 4                    | 0.04                 | 0.96                 |
| 5                    | 0.05                 | 0.95                 |
| 6                    | 0.06                 | 0.94                 |
| 7                    | 0.07                 | 0.93                 |
| 8                    | 0.08                 | 0.92                 |
| 9                    | 0.09                 | 0.91                 |
| 10                   | 0.10                 | 0.90                 |
| 20                   | 0.20                 | 0.80                 |
| 30                   | 0.30                 | 0.70                 |
| 40                   | 0.40                 | 0.60                 |
| 50                   | 0.50                 | 0.50                 |
| 60                   | 0.60                 | 0.40                 |
| 70                   | 0.70                 | 0.30                 |
| 80                   | 0.80                 | 0.20                 |
| 90                   | 0.90                 | 0.10                 |
| 100                  | 1.00                 | 0                    |

The Eu$^{3+}$/Lu$^{3+}$ ratios in the heterometallic europium(III)–lutetium(III) terephthalates were confirmed using energy-dispersive X-ray spectroscopy (EDX) (EDX spectrometer EDX-800P, Shimadzu, Japan) (Table 4). The Eu/Lu ratios measured via EDX were consistent with the ratios of Eu$^{3+}$/Lu$^{3+}$ taken for the synthesis in the form of EuCl$_3$ and LuCl$_3$ aqueous solutions (Table 3). The X-ray powder diffraction (XRD) measurements were performed on a D2 Phaser (Bruker, USA) X-ray diffractometer using Cu K$_{\alpha}$ radiation ($\lambda = 1.54056$ Å). The thermogravimetry curves were obtained using a TG 209 F1 Libra thermo-microbalance (Netzsch, Germany). The luminescence spectra were recorded with a Fluoromax-4 fluorescence spectrometer (Horiba Jobin Yvon, Japan). Lifetime measurements were performed with the same spectrometer using a pulsed Xe lamp (pulse duration: 3 μs). The absolute values of the photoluminescence quantum yields were recorded using a Fluorolog 3 Quanta-phi device. All measurements were performed at 25 °C.

Table 4. Eu$^{3+}$ atomic fraction (relative to the total amount of Eu$^{3+}$ and Lu$^{3+}$) in heterometallic europium(III)–lutetium(III) terephthalates taken during synthesis and obtained from EDX data.

| $\chi_{\text{Eu}}$ (%) | $\chi_{\text{Eu}}$ (%) | EDX  |
|------------------------|------------------------|------|
| 0                      | 0                      | 0.20 ± 0.21 |
| 2                      | 3.9 ± 0.4              |
| 4                      | 4.7 ± 0.5              |
| 5                      | 6.3 ± 0.6              |
| 6                      | 10.2 ± 1.0             |
| 10                     | 19.3 ± 1.9             |
| 20                     | 37 ± 4                 |
| 40                     | 80 ± 8                 |
| 100                    | 100                    |
4. Conclusions

In this work, we reported on the photoluminescence properties of luminescent antenna MOF—heterometallic europium(III)–lutetium(III) terephthalates. The series of (Eu<sub>x</sub>Lu<sub>1−x</sub>)<sub>2</sub>bdc<sub>3</sub>, nH<sub>2</sub>O (x = 0–1) was synthesized in the aqueous solution. At Eu<sup>3+</sup> concentrations of 1–40 at %, the heterometallic europium(III)–lutetium(III) terephthalates were formed as a mixture of the (Eu<sub>x</sub>Lu<sub>1−x</sub>)<sub>2</sub>bdc<sub>3</sub> and (Eu<sub>x</sub>Lu<sub>1−x</sub>)<sub>2</sub>bdc<sub>3</sub>:4H<sub>2</sub>O crystalline phases. At higher Eu<sup>3+</sup> concentrations, a single crystalline phase was formed: (Eu<sub>x</sub>Lu<sub>1−x</sub>)<sub>2</sub>bdc<sub>3</sub>:4H<sub>2</sub>O. All the synthesized samples containing Eu<sup>3+</sup> demonstrated a bright red emission corresponding to the <sup>5</sup>D<sub>0</sub>–<sup>7</sup>F<sub>2</sub> (J = 0–4) transitions of Eu<sup>3+</sup> ions upon 280 nm excitation into the singlet electronic excited state of terephthalate ions. An analysis of the fine structure of the emission spectra allowed us to conclude that the Eu<sup>3+</sup> ions were unevenly distributed between the Ln<sub>2</sub>bdc<sub>3</sub> and Ln<sub>2</sub>bdc<sub>3</sub>:4H<sub>2</sub>O phases: the Ln<sub>2</sub>bdc<sub>3</sub>:4H<sub>2</sub>O crystalline phase was enriched by Eu<sup>3+</sup> ions. The local symmetry of the Eu<sup>3+</sup> ions in the heterometallic Eu-Lu terephthalates was proposed based on a careful analysis of the fine structure of the emission spectra and the structural data. We demonstrated that the <sup>5</sup>D<sub>0</sub> excited state lifetimes were 4–4.8 times larger for Eu<sup>3+</sup> in the Ln<sub>2</sub>bdc<sub>3</sub> crystalline phase than in Ln<sub>2</sub>bdc<sub>3</sub>:4H<sub>2</sub>O due to the absence of luminescence quenching of the Eu<sup>3+</sup> by coordinated water molecules. The luminescence quantum yields of terephthalate ions decreased with an increase in the europium concentration from 2 to 100 at % Eu<sup>3+</sup> (λ<sub>ex</sub>. = 280 nm).

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**Sample Availability:** Samples of the reported compounds are available from the authors.

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