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Luminescent properties and thermal stability of $(Lu_{0.98}Eu_{0.02})_2bdc_3 \cdot 10H_2O$ metal–organic frameworks

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Materials and Methods

Benzene-1,4-dicarboxylic (terephthalic, H_2bdc) acid (>98%), sodium hydroxide (>99%), nickel(II) chloride hexahydrate (>99%), EDTA disodium salt (0.05M aqueous solution), and murexide were purchased from Sigma-Aldrich Chemie GmbH (Taufkirchen, Germany) and used without additional purification. Lutetium (III) and terbium (III) chlorides hexahydrates were purchased from Chemcraft (Kaliningrad, Russia). The synthesis of compound **1** was performed in the aqueous solution at the room temperature. 10 mL of 0.2 M sodium terephthalate solution was added dropwise at the vigorous stirring to the solution obtained by mixing of 4.9 mL of 0.2M $LuCl_3$ and 0.1 mL of 0.2M $EuCl_3$. The solid precipitates of the Eu-Lu terephthalate MOFs were separated from the reaction mixture via centrifugation (2300 g), washed with deionized water for 3 times, and kept under water for 24 hours. The obtained suspension of compound was centrifugated, decantated, and dried in air for 48 hours at a temperature of 20°C. Compound **2** was obtained by calcination of compound **1** under at 200 ^{0}C during 24 hours.

For **1**: yield 0.427 g (84%). Found (%): C, 28.10; H, 3.13; Lu, 98.05; Eu, 1.95. Calc. for $C_{24}H_{32}O_{22}Lu_{1.96}Eu_{0.04}$ (%): C, 27.77; H, 3.14; Lu, 98.00; Eu, 2.00. IR (ATR, ν/cm-1): 3373, 3231 (ν_s(O-H), 1664, 1558, 1507 (COO^-_{as}), 1386, 1314 (COO^-_s).

For **2**: yield 0.351 g (84%). Found (%): C, 32.10; H, 2.30; Lu, 97.98; Eu, 2.02. Calc. for $C_{24}H_{12}O_{12}Lu_{1.96}Eu_{0.04}$ (%): C, 32.25; H, 2.23; Lu, 98.00; Eu, 2.00. IR (ATR, ν/cm-1): 1538, 1505 (COO^-_{as}), 1394, 1316 $\nu_s(COO^-_s)$.

The relative content of the rare earth elements in the synthesized compounds was confirmed by energy-dispersive X-ray spectroscopy (EDX) (EDX spectrometer EDX-800P, Shimadzu, Japan) Powder X-ray diffraction (PXRD) measurements were performed on a D2 Phaser (Bruker, Billerica, MA, USA) Xray diffractometer using Cu Ka radiation (λ = 1.54056 Å). The thermal behavior of the compounds was studied by means of thermogravimetry using a Thermo-microbalance TG 209 F1 Libra (Netzsch, Selb, Germany) with a heat-up rate of 10 ◦C/min. IR spectra were measured using IRAffinity-1 spectrometer

with ATR module (Shimadzu, Japan) To carry out photoluminescence studies, the synthesized samples (20 mg) and potassium bromide (300 mg) were pressed into pellets (diameter 13 mm). The photoluminescence measurements spectra were recorded on Fluorolog-3 fluorescence spectrometer (Horiba Jobin Yvon, Kyoto, Japan).

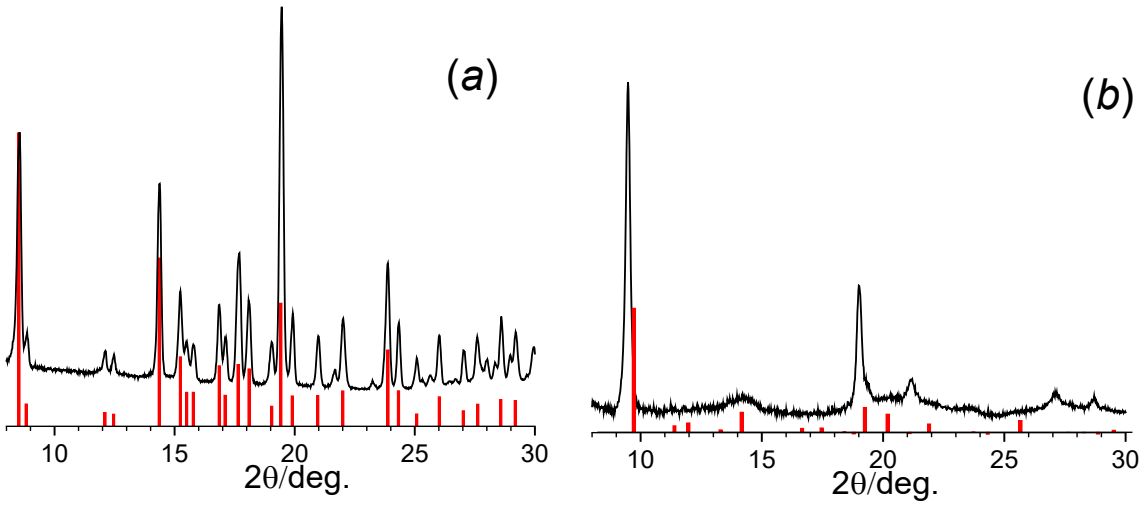

Figure S1 PXRD patterns of MOFs **1**(a) and **2**(b) are shown as lines. PXRD patterns of $Lu_2bdc_3 \cdot 10H_2O$[S1] (a) and Tb_2bdc_3[S2] simulated from the single-crystals structures are shown as bars.

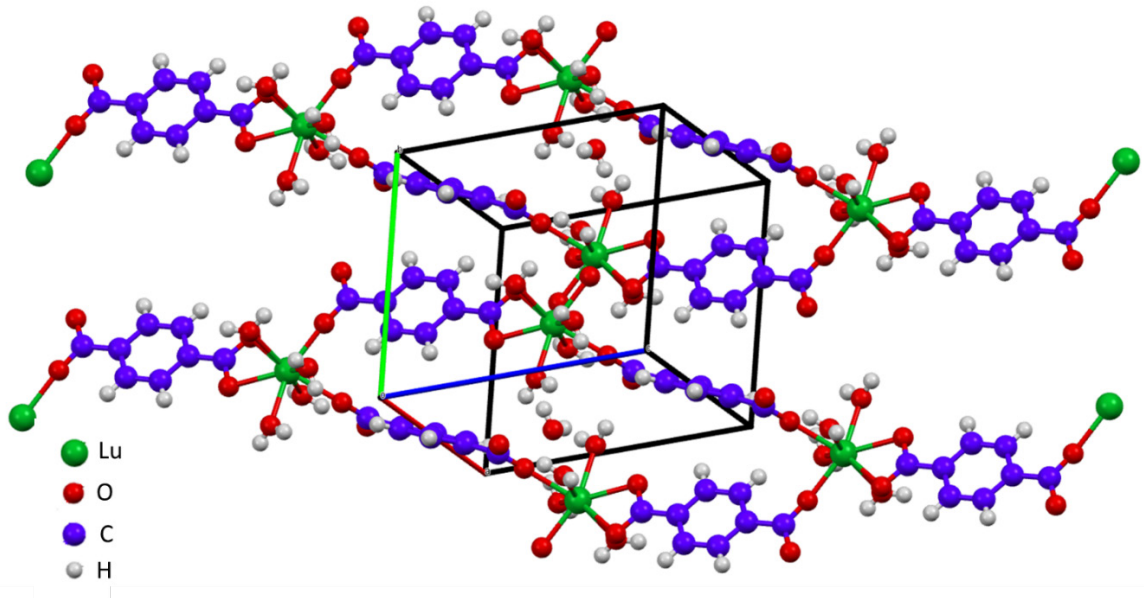

Figure S2 Structure of $Lu_2bdc_3 \cdot 10H_2O$ reconstructed from the cif file in ref. [S1]

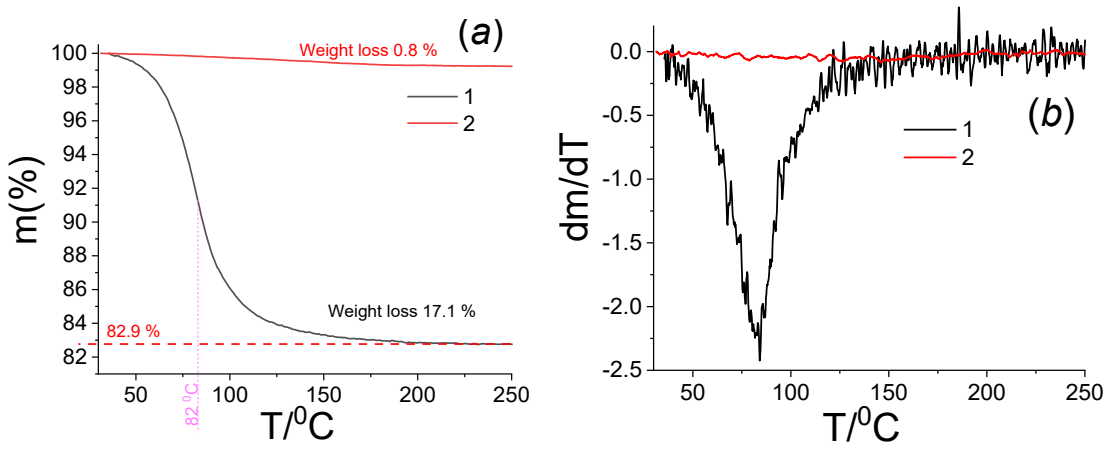

Figure S3 Thermogravimetric curve(a) and its first derivative (b) measured for MOF **1** and **2** at the temperature range 25-250 ^{0}C.

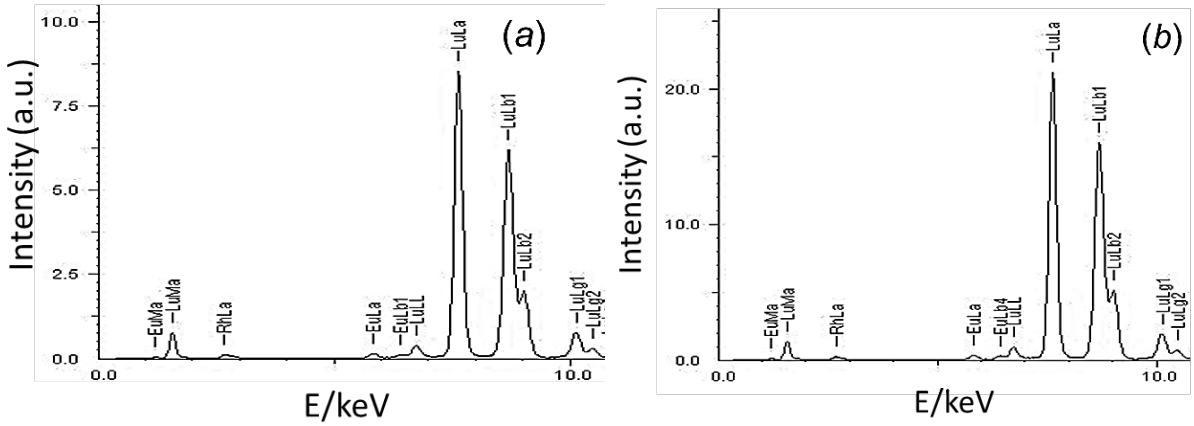

Figure S4 EDX spectra of MOFs **1**(a) and **2**(b).

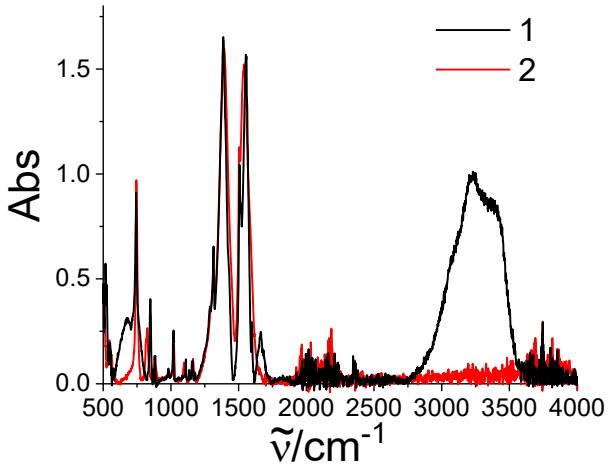

Figure S5 Infrared spectra of MOFs **1** and **2.**

The measurement of photophysical properties (photoluminescence decay time constants (τ_1 and τ_2); radiative (A_r), nonradiative (A_{nr}) and total (A_{tot}) decay rates, quantum efficiencies ($\phi(^5D_0)$), and formation quantum yields of the $^5D_0$ level; photoluminescence quantum yields (*PLQY*); asymmetric ratios (R_{21}).

Due to the different nature of the f-f transitions of Eu^{3+} ions, it can be used as a structural probe.[S3,S4] The probability of hypersensitive $^5D_0$-$^7F_2$ forced electric dipole transition is strongly affected by the local environment of the europium ion, whereas the probability of $^5D_0$-$^7F_1$ magnetic dipole transition intensity is significantly less sensitive to changes in the Eu^{3+} coordination sphere. The analysis of the asymmetry ratio R_{21}, which is equal to the ratio of the integral intensity of the bands corresponding to these transitions ($^5D_0$-$^7F_2$)/($^5D_0$-$^7F_1$), allows tracking of changes in the local environment of the europium (III) ions.[S5,S6]

Photoluminescence decay curves were fitted by the double exponential functions: $I(t) = I_1 \cdot e^{-\frac{t}{\tau_1}} + I_2 \cdot e^{-\frac{t}{\tau_2}}$, where τ_1 and τ_2 are decay time constants. Average luminescence lifetime (τ_{av}), which corresponds to the $^5D_0$ level lifetime, was calculated according to the following equation:[S7,S8]

$\tau_{av} = \frac{I_1\tau_1^2+I_2\tau_2^2}{I_1\tau_1+I_2\tau_2}$. Luminescence decay is affected by the combination of radiative and nonradiative processes. Radiative decay rate is determined by dipole transition strength and local-field correction. Nonradiative processes include multiphonon relaxation, quenching on impurities (e.g. O-H group of water molecules) and cooperative processes (cross-relaxation, energy migration).[S5,S9] Radiative and nonradiative decay rates of Eu^{3+}-doped phosphors can be calculated from the emission spectrum using the 4f–4f intensity theory.[S10] Magnetic dipole $^5D_0$–$^7F_1$ transition probability $A_{0\text{-}1} = A_{MD,0} \cdot n_0^3 = 14.65 \cdot 1.5^3 = 49\ s^{-1}$. $A_{MD,0}$ is the spontaneous emission probability of the magnetic dipole $^5D_0$–$^7F_1$, 14.65 s^{-1}, and n_0 is the refractive index, 1.5.[S11] Radiative decay rates $A_{0-\lambda}$ ($\lambda = 2, 4$) of the $^5D_0$–$^7F_\lambda$ emission transition can be obtained from formula:

$A_{0-\lambda} = A_{0-1}\frac{\nu_{0-1}}{\nu_{0-\lambda}}\frac{I_{0-\lambda}}{I_{0-1}}$, where $I_{0-\lambda}$ and $\nu_{0-\lambda}$ are integral intensity and frequency of the $^5D_0$–$^7F_\lambda$ emission transition. The total radiative decay rate, A_r, could be calculated by summing all the $A_{0-\lambda}$ radiative decay rates ($\lambda = 1, 2, 4$). The total decay rate is reciprocal to the observed lifetime of $^5D_0$ level $A_{tot} = \frac{1}{\tau_{av}}$, while nonradiative probability can be calculated as $A_{nr} = A_{tot} - A_r$. Quantum efficiency of $^5D_0$ level is $\phi(^5D_0) = \frac{A_r}{A_{tot}}$. To estimate the efficiency of the energy transfer from terephthalate ion to Eu^{3+}, we calculated quantum yield of $^5D_0$ level formation as $\Phi_{form}(^5D_0) = PLQY/\phi(^5D_0)$.

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