Multi-Functional Metal-Organic Frameworks Assembled from a Tripodal Organic Linker

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1. Characterization of the Organic PBU

1.1 – Hexaethyl(benzene-1,3,5-triyltris(methylene))tris(phosphonate)

Figure S1. $^{13}$C NMR spectrum of the intermediate molecule hexaethyl(benzene-1,3,5-triyltris(methylene))tris(phosphonate) in CDCl$_3$. 

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1.2 – (Benzene-1,3,5-triyltris(methylene))triposphonic Acid

**Figure S2.** $^1$H NMR spectrum of the target molecule (benzene-1,3,5-triyltris(methylene))triposphonic acid in DMSO-$d_6$. 
Figure S3. $^{13}$C NMR spectrum of the target molecule (benzene-1,3,5-triyltri(methylene))triphosphonic acid in DMSO-$d_6$. 
Figure S4. $^{31}$P NMR spectrum of the target molecule (benzene-1,3,5-triyltris(methylene))triphosphonic acid in DMSO-$d_6$. 
2. Milder Hydrothermal Synthetic Conditions

**Figure S5.** SEM images of the crystal morphology of the $[\text{La}_2(\text{Hbmt})_2(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}$ (1) material prepared at mild temperatures (100 ºC).
3. Electron Microscopy Studies: EDS Mapping

3.1 – [(La$_{0.95}$Eu$_{0.05}$)$_2$H$_3$bmt)$_2$(H$_2$O)$_2$]$\cdot$H$_2$O

Figure S6. Electron microscopy EDS mapping studies of a portion of the [(La$_{0.95}$Eu$_{0.05}$)$_2$H$_3$bmt)$_2$(H$_2$O)$_2$]$\cdot$H$_2$O (5) material.
3.2 – [(La$_{0.95}$Tb$_{0.05}$)$_2$(H$_3$bmt)$_2$(H$_2$O)$_2$]·H$_2$O

**Figure S7.** Electron microscopy EDS mapping studies of a portion of the [(La$_{0.95}$Tb$_{0.05}$)$_2$(H$_3$bmt)$_2$(H$_2$O)$_2$]·H$_2$O (6) material.
4. Solid-State NMR: \([\text{La}_2(\text{H}_3\text{bmt})_2(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}\)

4.1 – \(^{13}\text{C}\{^1\text{H}\}\) CP MAS

Figure S8. \(^{13}\text{C}\{^1\text{H}\}\) CP MAS spectrum of \([\text{La}_2(\text{H}_3\text{bmt})_2(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}\) (1). Spinning sidebands are depicted by an asterisk.
4.2 – $^{31}$P MAS

Figure S9. $^{31}$P MAS spectrum of [La$_2$(H$_3$btmt)$_2$(H$_2$O)$_2$].H$_2$O (I). Spinning sidebands are depicted by an asterisk. Peak deconvolution and integration throughout the entire spectral range (i.e., including the spinning sidebands) gives a ratio of ca. 1.00 : 1.04 : 1.01 for the isotropic resonances at ca. 15.3, 19.7 and 23.4 ppm, respectively, which is in perfect agreement with the crystal structure determination of the same material.
5. FT-IR Spectroscopy

Figure S10. FT-IR spectra of the [Ln₂(H₃bmt)₂(H₂O)₂]·H₂O materials [where Ln³⁺ = La³⁺ (1), Ce³⁺ (2), Pr³⁺ (3), Nd³⁺ (4), (La₀.95Eu₀.05)³⁺ (5) and (La₀.95Tb₀.05)³⁺ (6)]. The most relevant and diagnostic bands associated with the structural features of the materials are depicted.
6. Thermogravimetry

Figure S11. Thermograms of the [Ln$_2$(H$_3$bmt)$_2$(H$_2$O)$_2$]·H$_2$O materials [where Ln$^{3+}$ = Ce$^{3+}$ (2), Pr$^{3+}$ (3), Nd$^{3+}$ (4), (La$_{0.95}$Eu$_{0.05}$)$_3$$^{3+}$ (5) and (La$_{0.95}$Tb$_{0.05}$)$_3$$^{3+}$ (6)].
7. Photoluminescence

7.1 – Eu$^{3+}$ Materials

![Figure S12](image_url)

$\tau_{\text{5-dehyd}} = 1.60 \pm 0.01 \text{ ms}$

$\tau_5 = 0.60 \pm 0.01 \text{ ms}$

**Figure S12.** $^5$D$_0$ decay curves of [(La$_{0.95}$Eu$_{0.05}$)$_2$(H$_3$bmt)$_2$(H$_2$O)$_2$]·H$_2$O (5) (black) and [(La$_{0.95}$Eu$_{0.05}$)(H$_3$bmt)] (5-dehyd) (red), acquired at 298 K while monitoring the emission at 611.5 and 612.1 nm, respectively. Curves were fitted by using single exponential decay functions. The excitation was performed at 393 nm.
7.2 – Tb$^{3+}$ Materials

**Figure S13.** Excitation spectra of $[(\text{La}_{0.95}\text{Tb}_{0.05})_2(\text{H}_3\text{bmt})_2(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}$ (6) (black line) and $[(\text{La}_{0.95}\text{Tb}_{0.05})(\text{H}_3\text{bmt})]$ (6-dehyd) (red line) at 298 K while monitoring the Tb$^{3+}$ emission at 542 nm.

**Figure S14.** Ambient temperature (298 K) emission spectra of $[(\text{La}_{0.95}\text{Tb}_{0.05})_2(\text{H}_3\text{bmt})_2(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}$ (6) and $[(\text{La}_{0.95}\text{Tb}_{0.05})(\text{H}_3\text{bmt})]$ (6-dehyd) with excitation at 280 nm: black line, 6 at ambient pressure; red line, 6 after dehydration (6-dehyd) at 450 K under a vacuum of $5\times10^{-6}$ mbar.
Figure S15. $^5$D$_4$ decay curves of $[(La_{0.95}Tb_{0.05})_2(H_3bmt)_2(H_2O)_2] \cdot H_2O$ (6) (black) and $[(La_{0.95}Tb_{0.05})(H_3bmt)]$ (6-dehyd) (red) acquired at 298 K while monitoring the emission at 542 nm. Data points were fitted using single exponential decay functions. The excitation was performed at 280 nm.
7.3 – La$^{3+}$ Material

**Figure S16.** Excitation and emission spectra of [La$_2$(H$_3$btme)$_2$(H$_2$O)$_2$]·H$_2$O (1) recorded at 12 K and 298 K. Stationary state spectra are depicted with solid lines; dashed lines represent time-resolved emission spectra. For the excitation spectra (stationary state) the emission was detected at 305 nm (black lines) and at 435 nm (blue lines). For the emission stationary state spectra (red lines) the excitation was fixed at 270 nm. Time-resolved emission spectra: dashed green line, initial delay 0.01 ms and integration time of 0.05 ms ($\lambda_{\text{Exc.}}=270$ nm); dashed black line, initial delay 0.2 ms and integration time of 30 ms ($\lambda_{\text{Exc.}}=270$ nm); dashed blue line, initial delay 0.2 ms and integration time of 30 ms ($\lambda_{\text{Exc.}}=310$ nm).
Figure S17. Time decay curves of [La₂(H₃bmt)₂(H₂O)₃]·H₂O (1) acquired at 12 K. (a) Green squares: fluorescence emission detected at 287 nm with the excitation fixed at 270 nm. (b) Black squares: phosphorescence emission detected at 385 nm with the excitation fixed at 270 nm. Blue circles: emission detected at 435 nm with excitation fixed at 300 nm. Green and black lines correspond to data fits using single exponential decay functions. The blue line corresponds to a data fit using a bi-exponential decay function. Please note: because the employed phosphorometer is unable to discriminate time values lower than 10 µs, the fitted fluorescence value and its error (calculated from the fit) can only be considered as a rough estimation of the real fluorescence lifetime.
7.4 – Quantum Efficiency and Coordinated Water Molecules Calculations

Based on the emission spectra, $^5D_0$ lifetimes and empirical radiative and non-radiative transition rates, the $^5D_0$ quantum efficiency, $q$, has been determined for compounds 5 and 5-dehyd, establishing the effect of the coordinated water molecules on the reduction of the emission efficiency. Assuming that only non-radiative and radiative processes are involved in the depopulation of the $^5D_0$ state, $q$ is given by:

$$q = \frac{k_r}{k_r + k_{nr}}$$  \hspace{1cm} (Eq. 1)

where $k_r$ and $k_{nr}$ are the radiative and non-radiative transition probabilities, respectively, and $k_{exp} = \tau_{exp}^{-1}$ is the experimental transition probability. The emission intensity, $I$, taken as the integrated intensity $S$ of the emission lines for the $^5D_0 \rightarrow ^7F_{0,0}$ transitions, is given by:

$$I_{i \rightarrow j} = \hbar \omega_{i \rightarrow j} A_{i \rightarrow j} N_i \equiv S_{i \rightarrow j}$$  \hspace{1cm} (Eq. 2)

where $i$ and $j$ represent the initial ($^5D_0$) and final ($^7F_{0,0}$) levels, respectively, $\hbar \omega_{i \rightarrow j}$ is the transition energy, $A_{i \rightarrow j}$ the Einstein coefficient of spontaneous emission and $N_i$ the population of the $^5D_0$ emitting level. Because the $^5D_0 \rightarrow ^7F_{5,6}$ transitions are not observed experimentally, their influence on the depopulation of the $^5D_0$ excited state may be neglected and, thus, the radiative contribution is estimated based only on the relative intensities of the $^5D_0 \rightarrow ^7F_{0,4}$ transitions. The emission integrated intensity, $S$, of the $^5D_0 \rightarrow ^7F_{0,4}$ transitions has been measured for compounds 5 and 5-dehyd at 298 K.

Because the $^5D_0 \rightarrow ^7F_1$ transition does not depend on the local ligand field of the Eu$^{3+}$ ions (due to its dipolar magnetic nature) it may be used as a reference for the whole spectrum, in vacuo $A(^5D_0 \rightarrow ^7F_1)=14.65$ s$^{-1}$, and $k_r$ is given by:

$$k_r = A_{0 \rightarrow 1} \frac{\hbar \omega_{0 \rightarrow 1}}{S_{0 \rightarrow 1}} \sum_{J=0}^{4} \frac{S_{0-J}}{\hbar \omega_{0-J}}$$  \hspace{1cm} (Eq. 3)

where $A_{0,J}$ is the Einstein coefficient of spontaneous emission between the $^5D_0$ and the $^7F_J$ levels. An average index of refraction of 1.5 was considered for both samples, leading to $A(^5D_0 \rightarrow ^7F_1)=50$ s$^{-1}$. The number of water molecules ($n_w$) coordinated to Eu$^{3+}$ and Tb$^{3+}$ may be determined using the empirical formula of Kimura & Kato (with an intrinsic error of ±0.25) using the ambient temperature lifetimes of the as-prepared and dehydrated materials:

$$n_w = A \left( \frac{1}{\tau_{exp}} \right) - B$$  \hspace{1cm} (Eq. 4)

where $A = 1.1$ and $B = 0.71$ for Eu$^{3+}$, and $A = 4.0$ and $B = 1.0$ for Tb$^{3+}$. 

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8. References


