Photoluminescent Layered Lanthanide-Organic Framework Based on a Novel Trifluorotriphosphonate Organic Linker

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Electronic Supporting Information

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1. Characterization of the organic molecules

1.1. NMR spectroscopy and mass spectrometry

1.1.1. 1,3,5-Tris(chloromethyl)-2,4,6-trifluorobenzene ($L^1$)

Fig. S1 $^1$H NMR spectrum of the intermediate molecule 1,3,5-tris(chloromethyl)-2,4,6-trifluorobenzene in CDCl$_3$. 
Fig. S2 $^{13}$C NMR spectrum of the intermediate molecule 1,3,5-tris(chloromethyl)-2,4,6-trifluorobenzene in CDCl$_3$. 
Fig. S3 $^{19}$F NMR spectrum of the intermediate molecule 1,3,5-tris(chloromethyl)-2,4,6-trifluorobenzene in CDCl$_3$. 
1.1.2. Hexaethyl((2,4,6-trifluorobenzene-1,3,5-triyl)tris(methylene))tris(phosphonate) ($L^2$)

**Fig. S4** $^1$H NMR spectrum of the intermediate molecule hexaethyl((2,4,6-trifluorobenzene-1,3,5-triyl)tris(methylene))tris(phosphonate) in CDCl$_3$. 

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**Fig. S5** $^{13}$C NMR spectrum of the intermediate molecule hexaethyl((2,4,6-trifluorobenzene-1,3,5-triyl)tris(methylene))tris(phosphonate) in CDCl$_3$. 

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**Fig. S6** $^{19}$F NMR spectrum of the intermediate molecule hexaethyl((2,4,6-trifluorobenzene-1,3,5-triyl)tris(methylene))tris(phosphonate) in CDCl$_3$. 
**Fig. S7** Mass spectrum of the intermediate molecule hexaethyl((2,4,6-trifluorobenzene-1,3,5-triyl)tris(methylene))tris(phosphonate).
1.1.3. ((2,4,6-Trifluorobenzene-1,3,5-triyl)tris(methylene))triphosphonic acid (H$_6$tftp)

Fig. S8 $^1$H NMR spectrum of the target molecule ((2,4,6-trifluorobenzene-1,3,5-triyl)tris(methylene))triphosphonic acid in DMSO-$d_6$. The asterisk identifies the presence of a small impurity, possibly corresponding to compound $L^2$. 
Fig. S9 $^{13}$C NMR spectrum of the target molecule ((2,4,6-trifluorobenzene-1,3,5-triy)tris(methylene))triphosphonic acid in DMSO-$d_6$. 
Fig. S10 $^{19}$F NMR spectrum of the target molecule ((2,4,6-trifluorobenzene-1,3,5-triy)tris(methylene))triphosphonic acid in DMSO-$d_6$. 
Fig. S11 $^{31}$P NMR spectrum of the target molecule ((2,4,6-trifluorobenzene-1,3,5-triyl)tris(methylene))triphosphonic acid in DMSO-$d_6$. 
Fig. S12 Mass spectrum of the target molecule ((2,4,6-trifluorobenzene-1,3,5-triy)tris(methylene))triphosphonic acid.
1.2. Crystal structures

1.2.1. Crystallographic details

Single crystals of 1,3,5-tris(chloromethyl)-2,4,6-trifluorobenzene ($L^1$), hexaethyl((2,4,6-trifluorobenzene-1,3,5-triyl)tris(methylene))tris-(phosphonate) ($L^2$) and ((2,4,6-trifluorobenzene-1,3,5-triyl)tris(methylene))triphosphonic acid (H$_6$ttfp) were manually harvested from the crystallization vials. Single-crystal X-ray diffraction data were collected, processed and corrected for absorption using identical procedures as those described in section 2.5 of the main text.

Structures were solved using the direct methods algorithm implemented in SHELXS-97,$^1$ which allowed the immediate location of most of the non-hydrogen atoms. The remaining non-hydrogen atoms were located from difference Fourier maps calculated from successive full-matrix least-squares refinement cycles on $F^2$ using SHELXL-97.$^{1a,2}$ All non-hydrogen atoms were refined anisotropically.

Hydrogen atoms belonging to the organic molecules were placed at their idealized positions around the parent atoms using appropriate HFIX 23 (–CH$_2$–), HFIX 137 (–CH$_3$ in $L^2$) and HFIX 147 (–OH in H$_6$ttfp) instructions in SHELXL. Hydrogen atoms associated with the water molecules of crystallization present in the crystal structure of H$_6$ttfp were directly located from difference Fourier maps and included in the final structural model with the O–H and H···H distances restrained to 0.95(1) and 1.55(1) Å, respectively, in order to ensure a chemically reasonable geometry for these moieties. All hydrogen atoms were included in subsequent refinement cycles in riding motion approximation with isotropic thermal displacements parameters ($U_{iso}$) fixed at 1.2×$U_{eq}$ (–CH$_2$–) or 1.5×$U_{eq}$ (–CH$_3$, –OH and H$_2$O) of the parent atoms.

For $L^1$ the last difference Fourier map synthesis showed the highest peak (0.500 eÅ$^{-3}$) and deepest hole (-0.446 eÅ$^{-3}$) located at 0.69 Å and 0.44 Å from Cl3, respectively. For $L^2$ the correspondent values were 0.529 and -0.608 eÅ$^{-3}$, located at 0.32 Å from C18 and 0.35 Å from H18A, respectively, and for H$_6$ttfp the correspondent values were 0.518 and -0.381 eÅ$^{-3}$, located at 0.70 Å from C1 and 0.48 Å from P2. Details of the crystal data and structure refinement parameters for $L^1$, $L^2$ and H$_6$ttfp are summarized in Table S1.

Crystallographic data (excluding structure factors) for the crystal structures of the new tripodal organic ligand H$_6$ttfp, and of the two intermediate molecules, reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. See CCDC deposition numbers in Table S1. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 2EZ, U.K. FAX: (+44) 1223 336033. E-mail: deposit@ccdc.cam.ac.uk.
Table S1 Crystal data collection and structure refinement details for the organic molecules \(L^1\), \(L^2\) and \(H_6\text{tftp}\).

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<th>(L^2)</th>
<th>(H_6\text{tftp})</th>
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\(a\) \(R_1 = \sum |F_o| - |F_c| / \sum |F_o|, \quad b\) \(wR_2 = \sqrt{\sum \left[ w(F_o^2 - F_c^2) \right]^2} / \sum w(F_o^2) \)

\(c\) \(w = 1/\left[ \sigma^2(F_o^2) + (mP)^2 + nP \right] \) where \(P = (F_o^2 + 2F_c^2)/3\)
1.2.2. 1,3,5-Tris(chloromethyl)-2,4,6-trifluorobenzene ($L^I$)

**Fig. S13** Molecular structure of 1,3,5-tris(chloromethyl)-2,4,6-trifluorobenzene ($L^I$) showing the atomic labeling scheme for all non-hydrogen atoms. Displacement ellipsoids are drawn at the 50% probability level.
1.2.3. Hexaethyl((2,4,6-trifluorobenzene-1,3,5-triyl)tris(methylene))tris-(phosphonate) ($L^2$)

Fig. S14 Molecular structure of hexaethyl((2,4,6-trifluorobenzene-1,3,5-triyl)tris(methylene))tris(phosphonate) ($L^2$) showing the atomic labeling scheme for all non-hydrogen atoms. Displacement ellipsoids are drawn at the 30% probability level.
1.2.4. ((2,4,6-Trifluorobenzene-1,3,5-triyl)tris(methylene))triphosphonic acid (H₆tftp)

Fig. S15 Molecular structure of ((2,4,6-trifluorobenzene-1,3,5-triyl)tris(methylene))-triphosphonic acid (H₆tftp) showing the atomic labeling scheme for all non-hydrogen atoms. Displacement ellipsoids are drawn at the 50% probability level.
2. Electron Microscopy Studies: EDS Mapping

2.1. [(La$_{0.95}$Eu$_{0.05}$)(H$_3$tftp)(H$_2$O)] (2)

Fig. S16 Electron microscopy EDS mapping studies of a portion of the mixed-lanthanide photoluminescent [(La$_{0.95}$Eu$_{0.05}$)(H$_3$tftp)(H$_2$O)] (2) material.
2.2. \([\text{La}_{0.95}\text{Tb}_{0.05})(\text{H}_3\text{tftp})(\text{H}_2\text{O})]\) (3)

**Fig. S17** Electron microscopy EDS mapping studies of a portion of the mixed-lanthanide photoluminescent \([\text{La}_{0.95}\text{Tb}_{0.05})(\text{H}_3\text{tftp})(\text{H}_2\text{O})]\) (3) material.
2.3. \([\text{La}_{0.94}\text{Eu}_{0.03}\text{Tb}_{0.03})(\text{H}_3\text{tftp})(\text{H}_2\text{O})]\) (4)

Fig. S18 Electron microscopy EDS mapping studies of a portion of the mixed-lanthanide photoluminescent \([(\text{La}_{0.94}\text{Eu}_{0.03}\text{Tb}_{0.03})(\text{H}_3\text{tftp})(\text{H}_2\text{O})]\) (4) material.
Fig. S19 Powder X-ray diffraction pattern of [La(H$_3$tfp)(H$_2$O)] (1) and [(La$_{0.94}$Eu$_{0.03}$Tb$_{0.03}$)(H$_3$tfp)(H$_2$O)] (4) materials prepared (under hydrothermal conditions) at 180 °C for 72 h.
3. Additional crystallographic representations: \([\text{La}(\text{H}_3\text{tftp})(\text{H}_2\text{O})]\]

**Fig. S20** Schematic representation of the asymmetric unit of \([\text{La}(\text{H}_3\text{tftp})(\text{H}_2\text{O})]\) (1) showing all non-hydrogen atoms represented as thermal ellipsoids drawn at 50% probability level and hydrogen atoms as small spheres with arbitrary radii. The coordination environments around the two crystallographically independent metal centers have been completed for the sake of clarity. For selected bond lengths and angles on the two \{LaO\textsubscript{7}\} monocapped trigonal prismatic coordination environments see Table 2 in the main manuscript. Symmetry transformations used to generate equivalent atoms: (i) \(-x, 2-y, 2-z\); (ii) \(-1+x, y, z\); (iii) \(1+x, y, z\); (iv) \(-x, 2-y, 1-z\).
4. Solid-State NMR: [La(H₃tftp)(H₂O)]

Fig. S21 $^{13}$C($^1$H) CP MAS spectrum of [La(H₃tftp)(H₂O)] (I). Spinning sidebands are denoted using an asterisk.
5. FT-IR Spectroscopy

Fig. S22 FT-IR spectra of the isotypical series of [Ln(H₃tftp)(H₂O)] materials [where Ln³⁺ = La³⁺ (1), (La₀.₉₅Eu₀.₀₅)³⁺ (2) and (La₀.₉₅Tb₀.₀₅)³⁺ (3)].
6. Thermogravimetry

Fig. S23 Thermogravimetric curves of the isotypical series of [Ln(H$_3$tftp)(H$_2$O)] materials [where Ln$^{3+}$ = La$^{3+}$ (1), (La$_{0.95}$Eu$_{0.05}$)$^{3+}$ (2) and (La$_{0.95}$Tb$_{0.05}$)$^{3+}$ (3)].
7. Photoluminescence

![Photoluminescence Spectra](image)

**Fig. S24** Excitation and emission UV fluorescence spectra of the H₆tftp ligand (magenta), [La(H₆tftp)(H₂O)] (1) (blue) and [(La₀.₉₅Eu₀.₀₅)(H₆tftp)(H₂O)] (2) (red) compounds recorded at ambient temperature. For the excitation spectra the emission was detected at 330 nm (dotted lines) while for the emission spectra (solid lines) the excitation was fixed at 265 nm.
Fig. S25 $^5$D$_0$ and $^5$D$_4$ decay curves of the mixed-lanthanide [(La$_{0.95}$Eu$_{0.05}$)(H$_3$tftp)(H$_2$O)] (2) (red line) and [(La$_{0.95}$Tb$_{0.05}$)(H$_3$tftp)(H$_2$O)] (3) (green line) materials acquired at ambient temperature (298 K), while monitoring the emission at 610 and 542 nm, respectively. Data have been fitted with single exponential decay functions. The excitation was performed at 393 and 376 nm for 2 and 3, respectively.
Fig. S26 UV/Vis emission spectra of [(La$_{0.94}$Eu$_{0.03}$Tb$_{0.03}$)(H$_3$tftp)(H$_2$O)] (4) recorded at ambient temperature (orange line) and at 12 K (black line). Excitation at 265 nm. The break in the graph indicates the second order excitation position.
Fig. S27 Excitation spectra of [(La$_{0.94}$Eu$_{0.03}$Tb$_{0.03}$)(H$_3$tftp)(H$_2$O)] (4) recorded at ambient temperature (296 K) while detecting the Eu$^{3+}$ and Tb$^{3+}$ emission at 616 and 542 nm, respectively.
Fig. S28 Visible emission spectra of [(La<sub>0.94</sub>Eu<sub>0.03</sub>Tb<sub>0.03</sub>)(H<sub>3</sub>tftp)(H<sub>2</sub>O)]<sub>4</sub> excited at 265 nm as a function of temperature. The inset shows the plot of the integrated intensity vs. temperature, and the corresponding fit after logarithmic linearization of the temperature and integrated emission intensities.
Fig. S29 CIE chromaticity diagram showing the location of the red, green and light green emission at ambient temperature from the \([\text{La}_{0.95}\text{Eu}_{0.05}(\text{H}_3\text{tftp})(\text{H}_2\text{O})]\) (2), 
\([\text{La}_{0.95}\text{Eu}_{0.05}(\text{H}_3\text{tftp})(\text{H}_2\text{O})]\) (3) and 
\([\text{La}_{0.94}\text{Eu}_{0.03}\text{Tb}_{0.03}(\text{H}_3\text{tftp})(\text{H}_2\text{O})]\) (4) materials, respectively, under 265 nm excitation. The inset shows a magnification of the CIE emission coordinates modifications observed for the mixed \(\text{Eu}^{3+}/\text{Tb}^{3+}\) sample 4 at distinct temperatures.
8. References
