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The effect of metal distribution on the luminescence properties of mixedlanthanide metal-organic frameworks

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1. General experimental details

H₄odip was synthesised using a previously reported method,^{S1} whereas europium nitrate was generated *in situ* from the oxide.^{S2} All other starting materials and solvents were purchased from commercial sources and were used without further purification.

Powder X-ray diffraction (PXRD) patterns were recorded on a Bruker AXS D8 Advance diffractometer with copper K α radiation of wavelength 1.5406 Å at 298 K. Samples were placed on a flat plate, and measured with a 2 θ range of 5-60°. The step size was 0.024° with time per step of 0.3 s. Samples for PXRD analysis were air dried at room temperature for 1 – 2 min.

The fluorescence behaviour was studied at room temperature using a LS 55 luminescence spectrometer with a R928 photomultiplier and a xenon discharge lamp. Samples were decanted from solution and dried at 120 °C for 30 min prior to being ground with a pestle and mortar.

SEM and EDX spectroscopy analysis was conducted on a JEOL 6480LV SEM with an Oxford Instrument EDX system with X-Act silicon drift detector.

2. Synthesis of [Ln(Hodip)(H₂O)]·*n*H₂O, 1-6

Synthetic methods to produce compounds **1-6** were similar, and the synthesis of $[Tb(Hodip)(H_2O)]\cdot 2H_2O$ is detailed here. $Tb(NO_3)_3\cdot 5H_2O$ (0.3 mmol, 0.129 g) and H_4odip (0.3 mmol, 0.105 g) were placed in a glass vial and dissolved in water (15 ml). The vial was sealed and heated to 85 °C for 48 h. Colourless, needle crystals were produced with a yield of 0.054 g (25 % based on H_4odip). The PXRD patterns for **1-6** are shown in Figure 2. Figure S1 shows the experimental PXRD pattern for **4** in comparison with that simulated from the crystal structure.



Figure S1. The experimental PXRD pattern for [Tb(Hodip)(H₂O)]·2H₂O **4**, in comparison with the PXRD pattern simulated from the crystal structure.

3. Synthesis of [Gd_{0.17}Tb_{0.19}Eu_{0.64}(Hodip)(H₂O)]·*n*H₂O, 7

Eu₂O₃ (0.099 mmol, 0.035 g) was added to water (15 ml), and whilst stirring, 1 M nitric acid was added dropwise until the pH of the solution was neutral. Tb(NO₃)₃·5H₂O (0.098 mmol, 0.043 g) and Gd(NO₃)₃·6H₂O (0.13 mmol, 0.062 g) were added to the solution along with H₄odip (0.303 mmol, 0.105 g). The vial was sealed and heated to 85 °C for 48 h. Colourless,

needle crystals were produced with a yield of 0.041 g (27 % based on H_4 odip). The PXRD pattern for 7 is shown in Figure S2.



Figure S2. The experimental PXRD pattern for $[Gd_{0.17}Tb_{0.19}Eu_{0.64}(Hodip)(H_2O)] \cdot nH_2O$ 7, in comparison with the PXRD pattern for $[Tb(Hodip)(H_2O)] \cdot 2H_2O$ 4.

The composition of 7 was investigated by EDX spectroscopy to determine the percentage of europium, gadolinium and terbium present in the crystals, the values of which have been normalised to equal a total of 100 %. The results are shown graphically in Figure S3.



Crystal	% Eu	% Tb	% Gd
1	62.0	19.3	18.7
2	63.9	19.9	16.2
3	63.7	19.5	16.8
4	65.7	18.9	15.4
5	64.2	19.4	16.4

Figure S3. The percentage of europium, terbium and gadolinium present in five crystals of the product as determined through EDX spectroscopy.

4. Synthesis of the core-shell materials 8-10

The core-shell MOFs were all synthesised using similar methods. The detailed synthesis of $[Gd(Hodip)(H_2O)]@[Tb(Hodip)(H_2O)]@[Eu(Hodip)(H_2O)]$ is provided here. Eu₂O₃ (0.298 mmol, 0.105 g) was added to water (15 ml). Whilst stirring, 1 M nitric acid was added dropwise until the pH of the solution was neutral. H₄odip (0.303 mmol, 0.105 g) was added, and the mixture was stirred until all materials had dissolved. The solution was placed in a sealed vial and heated to 85 °C for 48 h. Colourless, needle crystals were produced which were washed with water through a process of decanting the supernatant and replacing with fresh water. This was repeated three times over 72 h. The crystals were placed in a solution of Tb(NO₃)₃·5H₂O (0.296 mmol, 0.129 g) and H₄odip (0.303 mmol, 0.105 g) in water (15 ml) and heated to 85 °C

for 48 h. Colourless crystals were produced and washed in the same way as the crystals isolated after the first step. These crystals were placed in a solution of $Gd(NO_3)_3 \cdot 5H_2O$ (0.292 mmol, 0.132 g) and H₄odip (0.303 mmol, 0.105 g) in water (15 ml) heated to 85 °C for 48 h. The colourless crystals produced were the core-shell product $[Gd(Hodip)(H_2O)]@[Tb(Hodip)(H_2O)]@[Eu(Hodip)(H_2O)]$ 8.

For the synthesis of $[Tb(Hodip)(H_2O)]@[Eu(Hodip)(H_2O)]@[Gd(Hodip)(H_2O)]$ the $[Gd(Hodip)(H_2O)]$ core was synthesised using the method detailed above. An aqueous solution containing dissolved Eu₂O₃ (0.302 mmol, 0.106 g) and HNO₃ (1 M solution) was added dropwise until the pH of the solution was neutral. The crystals of $[Gd(Hodip)(H_2O)]$ were added to the solution and it was placed in a sealed vial and heated to 85 °C for 48 h. The resulting crystals were placed in an aqueous solution of $Tb(NO_3)_3 \cdot 5H_2O$ (0.340 mmol, 0.147 g) and H₄odip (0.303 mmol, 0.105 g) and heated to 85 °C for 48 h. Colourless crystals of the core-shell product $[Tb(Hodip)(H_2O)]@[Eu(Hodip)(H_2O)]@[Gd(Hodip)(H_2O)]$ were formed and washed as described for **8**.

The synthesis of $[Eu(Hodip)(H_2O)]@[Gd(Hodip)(H_2O)]@[Tb(Hodip)(H_2O)]$ **10** was carried out in a similar manner, but altering the ordering of the reagents.

The PXRD patterns for compounds **8-10** are shown in Figure S4, and SEM images of **8-10** are shown in Figure S5.



Figure S4. PXRD patterns for the core-shell MOFs **8-10** in comparison with that observed for [Tb(Hodip)(H₂O)]·2H₂O **4**.



Figure S5. SEM images for the core-shell MOFs (a) 8, (b) 9 and (c) 10.

The compositions of **8-10** were investigated by EDX spectroscopy to determine the percentage of europium, gadolinium and terbium present in the crystals, the values of which have been normalised to equal a total of 100 %. The results are shown graphically in Figure S6.



Crystal	% Eu	% Tb	% Gd
1	2.4	6.5	91.1
2	3.4	12.8	83.8
3	4.7	22.6	72.7
4	3.7	15.1	81.2

Crystal	% Eu	% Tb	% Gd	
1	7.2	92.2	0.6	
2	18.1	80.9	1.0	
3	6.4	92.8	0.8	
4	8.6	91.1	0.3	

Crystal	% Eu	% Tb	% Gd
1	92.6	1.4	6.0
2	86.3	2.6	11.1
3	87.3	2.1	10.6
4	84.7	2.3	13.0
5	75.1	1.5	23.4

Figure S6. The percentages of Eu, Tb and Gd observed in core-shell crystals of (a) 8 (b) 9 and (c) 10 as observed by EDX analysis.

5. Analysis of a mixture of 2, 3 and 4

The physical mixture of $[Eu(Hodip)(H_2O)] \cdot nH_2O$ **2**, $[Gd(Hodip)(H_2O)] \cdot 2H_2O$ **3** and $[Tb(Hodip)(H_2O)] \cdot 2H_2O$ **4** was analysed by SEM, as shown in Figure S7.



Figure S7. Scanning electron microscope (SEM) image of physical mixture of [Eu(Hodip)(H₂O)]·*n*H₂O **2** (red), [Gd(Hodip)(H₂O)]·2H₂O **3** (blue) and [Tb(Hodip)(H₂O)]·2H₂O (green), as identified by EDX analysis.

6. Crystallography

Single crystal X-ray structural analyses were carried out on $[Sm(Hodip)(H_2O)] \cdot 1.65H_2O$ **1**, $[Gd(Hodip)(H_2O)] \cdot 2H_2O$ **3**, $[Tb(Hodip)(H_2O)] \cdot 2H_2O$ **4**, $[Dy(Hodip)(H_2O)] \cdot 1.8H_2O$ **5**, $[Er(Hodip)(H_2O)] \cdot 1.8H_2O$ **6** and $H_4odip \cdot H_2O$. Suitable crystals were selected and mounted on a SuperNova, Dual, Cu at zero, EosS2 diffractometer. Using the Olex2 interface,^{S3} the structures were solved with ShelXS^{S4} and refined using ShelXL.^{S5} Details of the data collections, solutions and refinements for the metal complexes are given in Table S1 and for $H_4odip \cdot H_2O$ in Table S2.

The structures of **1** and **3-6** contain two water molecules per asymmetric unit, one of which is disordered over two positions. The occupancies of these solvent molecules differ between structures.

The samarium-containing structure 1 contains O(11) with a site occupancy of 65 % and O(12) which is disordered over two sites, O(12) and O(12A), with site occupancies of 65 % and 35 % respectively. The structure therefore contains a total solvent content of 1.65 water molecules per samarium.

The crystals of **3** were very obviously twinned. Thus, integration of the data for the sample took account of a 2-component twin by virtue of a 180° rotation about the 1,0,0 reciprocal direction. The refined twin fractions had a ratio of 75:25. The disordered water molecule based on O(12) and O(12A) was disordered over 2 sites with site occupancies of 80 % and 20 % respectively.

The asymmetric unit of the dysprosium-containing structure **5** contains O(11) with a site occupancy of 80 % based on electron density whilst the O(12)/O(12A) disordered water molecule was modelled with a site occupancy ratio of 75:25. A total of 1.8 solvent water molecules are therefore present per dysprosium.

The water molecule based on O(11) in the structure of **6** was modelled to take account of 80:20 disorder over 2 sites. O(12) refined to 100 % occupancy and, therefore, the structure of **6** contains a total solvent content of 1.8 water molecules per erbium centre.

Compound	1	3	4	5	6
Empirical formula	C ₁₆ H _{12.3} O _{11.65} Sm	C ₁₆ H ₁₃ GdO ₁₁	$C_{16}H_{13}O_{11}Tb$	C ₁₆ H _{12.6} DyO _{11.8}	C ₁₆ H _{12.6} ErO _{11.8}
Formula weight	541.31	554.51	556.18	556.16	560.92
Temperature/K	150.00(10)	150.00(10)	150.01(10)	150.00(10)	150.01(10)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_{1}/n$	$P2_{1}/n$	$P2_1/n$	$P2_1/n$	$P2_{1}/n$
a/Å	9.92621(12)	9.8450(5)	9.8243(2)	9.8077(2)	9.76631(17)
b/Å	12.74029(16)	12.7548(6)	12.7350(3)	12.7197(3)	12.7056(2)
c/Å	13.9980(2)	13.9951(8)	13.9772(3)	13.9411(4)	13.9075(2)
$\beta/^{\circ}$	93.8694(12)	93.753(5)	93.8140(19)	93.756(2)	93.7181(16)
Volume/Å ³	1766.19(4)	1753.62(16)	1744.85(7)	1735.42(8)	1722.10(5)
Ζ	4	4	4	4	4
$\rho_{\rm calc} {\rm g/cm}^3$	2.036	2.100	2.117	2.129	2.163
μ/mm^{-1}	25.589	25.113	20.585	23.679	9.694
<i>F</i> (000)	1054.0	1076.0	1080.0	1076.0	1084.0
Crystal size/mm ³	$0.079 \times 0.058 \times 0.042$	$0.078 \times 0.019 \times 0.015$	$0.079 \times 0.054 \times 0.029$	0.056 × 0.032 × 0.025	$0.111 \times 0.046 \times 0.019$
Radiation	$CuK\alpha (\lambda = 1.54184 \text{ Å})$	Cu <i>K</i> α (λ = 1.54184 Å)	Cu <i>K</i> α (λ = 1.54184 Å)	Cu <i>K</i> α (λ = 1.54184 Å)	$CuK\alpha (\lambda = 1.54184 \text{ Å})$
2θ range for data collection/°	9.396 to 145.918	9.39 to 145.7	9.404 to 145.672	9.422 to 145.704	9.438 to 145.298
	$-12 \le h \le 12,$	$-12 \le h \le 10,$	$-11 \le h \le 12,$	$-10 \le h \le 12,$	$-9 \le h \le 11,$
Index ranges	$-15 \le k \le 15,$	$-15 \le k \le 15,$	$-15 \le k \le 8,$	$-15 \le k \le 9,$	$-15 \le k \le 9,$
	$-16 \le l \le 17$	$-17 \le l \le 17$	$-17 \le l \le 17$	$-16 \le l \le 17$	$-16 \le l \le 16$
Reflections collected	26509	5691	7002	6659	5971
Independent reflections, $R_{\rm int}$	3504, 0.0294	5691, 0.0252	3383, 0.0304	3377, 0.0324	3336, 0.0252
Data/restraints/parameters	3504/1/270	5691/6/279	3383/1/270	3377/0/278	3336/0/276
Goodness-of-fit on F^2	1.069	0.893	1.143	1.014	1.060
Final R1, wR2 indexes $[I \ge 2\sigma(I)]$	0.0219, 0.0531	0.0282, 0.0695	0.0382, 0.0789	0.0299, 0.0610	0.0311, 0.0749
Final <i>R</i> 1, <i>wR</i> 2 indexes [all data]	0.0241, 0.0542	0.0419, 0.0718	0.0460, 0.0824	0.0407, 0.0652	0.0378, 0.0792
Largest diff. peak/hole / e Å ⁻³	0.46/-0.72	0.83/-0.60	0.54/-0.56	0.62/-0.52	0.66/-0.64

 Table S1. Crystallographic data for compounds 1, 3-6.

Empirical formula	$C_{16}H_{12}O_{10}$
Formula weight	364.26
Temperature/K	150.00(10)
Crystal system	triclinic
Space group	PĪ
a/Å	7.7677(7)
b/Å	8.5957(6)
c/Å	12.8044(10)
<i>α</i> /°	73.373(7)
$\beta/^{\circ}$	72.777(8)
$\gamma/^{\circ}$	70.317(7)
Volume/Å ³	752.19(12)
Ζ	2
$\rho_{\rm calc} g/{\rm cm}^3$	1.608
μ/mm^{-1}	1.193
<i>F</i> (000)	376.0
Crystal size/mm ³	$0.114 \times 0.084 \times 0.06$
Radiation	$CuK\alpha$ ($\lambda = 1.54184$)
2θ range for data collection/°	7.388 to 145.612
Index ranges	$-9 \le h \le 8,$ $-10 \le k \le 10,$ $-15 \le l \le 15$
Reflections collected	4848
Independent reflections, $R_{\rm int}$	2910, 0.0230
Data/restraints/parameters	2910/0/199
Goodness-of-fit on F^2	1.041
Final R1, wR2 indexes $[I \ge 2\sigma(I)]$	0.0408, 0.1058
Final R1, wR2 indexes [all data]	0.0481, 0.1139
Largest diff. peak/hole / e Å ⁻³	0.29/-0.27

Table S2. Crystallographic data for H40dip·H2O.

The molecular structure of H_4 odip is shown in Figure S8(a), with one of the principal hydrogen bonding motifs and the gross structure depicted in Figures S8(b) and S8(c) respectively.



Figure S8. The structure of H₄odip·H₂O, showing (a) the molecular structure, (b) one of the main hydrogen bonding motifs (a $R_3^3(10)$ ring), and (c) the gross structure, with one H₄odip molecule highlighted in purple.

7. References

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