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

Laura K. Cadman, Mary F. Mahon and Andrew D. Burrows

Electronic supplementary information

1. General experimental details S2
2. Synthesis of [Ln(Hodip)(H2O)]·nH2O, 1-6 S2
3. Synthesis of [Gd0.17Tb0.19Eu0.64(Hodip)(H2O)]·nH2O, 7 S2
4. Synthesis of the core-shell materials 8-10 S3
5. Analysis of a mixture of 2, 3 and 4 S5
6. Crystallography S6
7. References S9

Electronic Supplementary Material (ESI) for Dalton Transactions. This journal is © The Royal Society of Chemistry 2018
1. **General experimental details**

H$_4$odip was synthesised using a previously reported method,\textsuperscript{S1} whereas europium nitrate was generated \textit{in situ} from the oxide.\textsuperscript{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$\alpha$ radiation of wavelength 1.5406 Å at 298 K. Samples were placed on a flat plate, and measured with a 2$\theta$ 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)(H$_2$O)]·nH$_2$O, 1-6**

Synthetic methods to produce compounds 1-6 were similar, and the synthesis of [Tb(Hodip)(H$_2$O)]·2H$_2$O is detailed here. Tb(NO$_3$)$_3$·5H$_2$O (0.3 mmol, 0.129 g) and H$_4$odip (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$_4$odip). 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.](image)

**Figure S1.** The experimental PXRD pattern for [Tb(Hodip)(H$_2$O)]·2H$_2$O 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)(H$_2$O)]·nH$_2$O, 7**

Eu$_2$O$_3$ (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(NO$_3$)$_3$·5H$_2$O (0.098 mmol, 0.043 g) and Gd(NO$_3$)$_3$·6H$_2$O (0.13 mmol, 0.062 g) were added to the solution along with H$_4$odip (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 H4odip). The PXRD pattern for 7 is shown in Figure S2.

![Figure S2. The experimental PXRD pattern for [Gd0.17:Tb0.19:Eu0.64(Hodip)(H2O)]nH2O 7, in comparison with the PXRD pattern for [Tb(Hodip)(H2O)]2H2O 4.](image)

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.

![Figure S3. The percentage of europium, terbium and gadolinium present in five crystals of the product as determined through EDX spectroscopy.](image)

### 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)(H2O)]@[Tb(Hodip)(H2O)]@[Eu(Hodip)(H2O)] 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$_3$)$_3$·5H$_2$O (0.292 mmol, 0.132 g) and H$_4$odip (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$_2$O)]@[Tb(Hodip)(H$_2$O)]@[Eu(Hodip)(H$_2$O)] 8.

For the synthesis of [Tb(Hodip)(H$_2$O)]@[Eu(Hodip)(H$_2$O)]@[Gd(Hodip)(H$_2$O)] the [Gd(Hodip)(H$_2$O)] core was synthesised using the method detailed above. An aqueous solution containing dissolved Eu$_2$O$_3$ (0.302 mmol, 0.106 g) and HNO$_3$ (1 M solution) was added dropwise until the pH of the solution was neutral. The crystals of [Gd(Hodip)(H$_2$O)] 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$_3$)$_3$·5H$_2$O (0.340 mmol, 0.147 g) and H$_4$odip (0.303 mmol, 0.105 g) and heated to 85 °C for 48 h. Colourless crystals of the core-shell product [Tb(Hodip)(H$_2$O)]@[Eu(Hodip)(H$_2$O)]@[Gd(Hodip)(H$_2$O)] 9 were formed and washed as described for 8.

The synthesis of [Eu(Hodip)(H$_2$O)]@[Gd(Hodip)(H$_2$O)]@[Tb(Hodip)(H$_2$O)] 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)(H$_2$O)]·2H$_2$O 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)(H₂O)]·nH₂O 2, [Gd(Hodip)(H₂O)]·2H₂O 3 and [Tb(Hodip)(H₂O)]·2H₂O 4 was analysed by SEM, as shown in Figure S7.
Figure S7. Scanning electron microscope (SEM) image of physical mixture of [Eu(Hodip)(H$_2$O)]·$\nu$H$_2$O 2 (red), [Gd(Hodip)(H$_2$O)]·2H$_2$O 3 (blue) and [Tb(Hodip)(H$_2$O)]·2H$_2$O (green), as identified by EDX analysis.

6. Crystallography

Single crystal X-ray structural analyses were carried out on [Sm(Hodip)(H$_2$O)]·1.65H$_2$O 1, [Gd(Hodip)(H$_2$O)]·2H$_2$O 3, [Tb(Hodip)(H$_2$O)]·2H$_2$O 4, [Dy(Hodip)(H$_2$O)]·1.8H$_2$O 5, [Er(Hodip)(H$_2$O)]·1.8H$_2$O 6 and H$_4$odip·H$_2$O. 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$_4$odip·H$_2$O 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.
Table S1. Crystallographic data for compounds 1, 3-6.

| Compound | 1            | 3       | 4       | 5          | 6           |
|----------|--------------|---------|---------|------------|-------------|
| Empirical formula | C_{16}H_{25}O_{11.6}Sm | C_{16}H_{17}GdO_{11} | C_{16}H_{17}O_{11}Tb | C_{16}H_{26}DyO_{11.8} | C_{16}H_{26}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) | 9.7663(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) |
| β/° | 93.8694(12) | 93.753(5) | 93.8140(19) | 93.756(2) | 93.7181(16) |
| Volume/Å³ | 1766.19(4) | 1753.62(16) | 1744.85(7) | 1735.42(8) | 1722.10(5) |
| Z | 4 | 4 | 4 | 4 | 4 |
| \(p_{\text{calc}}\)/g/cm³ | 2.036 | 2.100 | 2.117 | 2.129 | 2.163 |
| \(\mu\)/mm⁻¹ | 25.589 | 25.113 | 20.585 | 23.679 | 9.694 |
| F(000) | 1054.0 | 1076.0 | 1080.0 | 1076.0 | 1084.0 |
| Crystal size/mm³ | 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 \(\times \) 0.032 \(\times \) 0.025 | 0.111 \(\times \) 0.046 \(\times \) 0.019 |
| Radiation | CuKα (\(\lambda = 1.54184\) Å) | CuKα (\(\lambda = 1.54184\) Å) | CuKα (\(\lambda = 1.54184\) Å) | CuKα (\(\lambda = 1.54184\) Å) | CuKα (\(\lambda = 1.54184\) Å) |
| 20 range for data collection/° | 9.396 to 145.919 | 9.39 to 145.7 | 9.404 to 145.672 | 9.422 to 145.704 | 9.438 to 145.298 |
| Index ranges | \(-12 \leq h \leq 12, -15 \leq k \leq 15, -16 \leq l \leq 17\) | \(-12 \leq h \leq 10, -15 \leq k \leq 15, -17 \leq l \leq 17\) | \(-11 \leq h \leq 12, -15 \leq k \leq 8, -17 \leq l \leq 17\) | \(-10 \leq h \leq 12, -15 \leq k \leq 9, -16 \leq l \leq 17\) | \(-9 \leq h \leq 11, -15 \leq k \leq 9, -16 \leq l \leq 16\) |
| Reflections collected | 26509 | 5691 | 7002 | 6659 | 5971 |
| Independent reflections, \(R_{\text{int}}\) | 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 \(P^2\) | 1.069 | 0.893 | 1.143 | 1.014 | 1.060 |
| Final \(R_1\), w\(R_2\) indexes \([I \geq 2\sigma(I)]\) | 0.0219, 0.0531 | 0.0282, 0.0695 | 0.0382, 0.0789 | 0.0299, 0.0610 | 0.0311, 0.0749 |
| Final \(R_1\), w\(R_2\) indexes \([\text{all data}]\) | 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 S2. Crystallographic data for H₄odip·H₂O.

| Property                      | Value                                      |
|-------------------------------|--------------------------------------------|
| Empirical formula            | C₁₆H₁₂O₁₀                                  |
| Formula weight               | 364.26                                     |
| Temperature/K                | 150.00(10)                                 |
| Crystal system               | triclinic                                  |
| Space group                   | P₁                                          |
| a/Å                          | 7.7677(7)                                  |
| b/Å                          | 8.5957(6)                                  |
| c/Å                          | 12.8044(10)                                |
| α/°                          | 73.373(7)                                  |
| β/°                          | 72.777(8)                                  |
| γ/°                          | 70.317(7)                                  |
| Volume/Å³                    | 752.19(12)                                 |
| Z                            | 2                                          |
| ρcalc/g/cm³                  | 1.608                                      |
| µ/mm⁻¹                       | 1.193                                      |
| F(000)                       | 376.0                                      |
| Crystal size/mm³             | 0.114 × 0.084 × 0.06                       |
| Radiation                    | CuKα (λ = 1.54184)                         |
| 2θ range for data collection/°| 7.388 to 145.612                           |
| Index ranges                 | −9 ≤ h ≤ 8, −10 ≤ k ≤ 10, −15 ≤ l ≤ 15   |
| Reflections collected        | 4848                                       |
| Independent reflections, R_int| 0.0230                                     |
| Data/restraints/parameters   | 2910/0/199                                 |
| Goodness-of-fit on F²        | 1.041                                      |
| Final R1, wR2 indexes        | 0.0408, 0.1058                             |
| [I ≥ 2σ(I)]                  |                                            |
| Final R1, wR2 indexes        | 0.0481, 0.1139                             |
| [all data]                   |                                            |
| Largest diff. peak/hole / e Å³| 0.29/-0.27                                |

The molecular structure of H₄odip 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 $\text{H}_4\text{o}dip \cdot \text{H}_2\text{O}$, showing (a) the molecular structure, (b) one of the main hydrogen bonding motifs (a $R_3^2(10)$ ring), and (c) the gross structure, with one $\text{H}_4\text{o}dip$ molecule highlighted in purple.

**7. References**

S1. Y. Peng, G. Li, J. Hua, Z. Shi and S. Feng, *CrystEngComm*, 2015, **17**, 3162.

S2. H. Wang, R. Wang, X. Sun, R. Yan and Y. Li, *Mater. Res. Bull.*, 2005, **40**, 911.

S3. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339.

S4. G. M. Sheldrick, *Acta Crystallogr. Sect. A*, 2008, **64**, 112.

S5. G. M. Sheldrick, *Acta Crystallogr. Sect. C*, 2015, **71**, 3.