Supporting Information

Engineering lanthanide-optical centres in IRMOF-3 by post-synthetic modification

Reda M. Abdelhameed,[a,b] Luis D. Carlos,[c] Artur M. S. Silva,*[b] and João Rocha*[a]

[a]Department of Chemistry, CICECO, University of Aveiro, 3810-193 Aveiro, Portugal.
[b]Department of Chemistry, QOPNA, University of Aveiro, 3810-193 Aveiro, Portugal.
[c]Department of Physics, CICECO, University of Aveiro, 3810-193 Aveiro, Portugal.

Table of contents

1. Elemental analysis 2
2. X-Ray diffraction 4
3. NMR analysis 6
4. FT-IR analysis 24
5. Scanning Electron Microscopy 28
6. Photoluminescence spectroscopy 30
1. Elemental analysis

Table S1. Elemental analysis of IRMOF-3-CA, Ln-IRMOF-3-CA, IRMOF-3-GL and Ln-IRMOF-3-GL (Ln = Nd, Eu) (%).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Metal &amp; chloride ratio *</th>
<th>Zn</th>
<th>Nd</th>
<th>Cu</th>
<th>C</th>
<th>H</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>IRMOF-3-CA</td>
<td>Zn$<em>4$C$</em>{40}$H$<em>{41}$N$</em>{7}$O$<em>{19}$ = [Zn$<em>4$(C$</em>{10}$H$</em>{22}$N$<em>8$O$</em>{19}$)$_2$,2(C$_6$H$_5$)$_2$N]</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>45.75 (45.63)</td>
<td>4.12 (4.07)</td>
</tr>
<tr>
<td>Nd-IRMOF-3-CA</td>
<td>Zn$<em>4$C$</em>{38}$H$_{43}$Cl$_3$Nd$<em>2$N$<em>2$O$</em>{19}$ = [Zn$<em>4$(C$</em>{10}$H$</em>{22}$N$<em>8$O$</em>{19}$)$_2$,2(C$_6$H$_5$)$_2$N]</td>
<td>39.44 ±1.61</td>
<td>30.10 ±2.52</td>
<td>-</td>
<td>30.46 ±1.91</td>
<td>18.91 (19.02)</td>
<td>2.89 (2.71)</td>
</tr>
<tr>
<td>Eu-IRMOF-3-CA</td>
<td>Zn$<em>4$C$</em>{38}$H$_{43}$Cl$_3$Eu$<em>2$N$<em>2$O$</em>{19}$ = [Zn$<em>4$(C$</em>{10}$H$</em>{22}$N$<em>8$O$</em>{19}$)$_2$,2(C$_6$H$_5$)$_2$N]</td>
<td>41.17 ±1.79</td>
<td>-</td>
<td>29.91 ±2.11</td>
<td>28.92 ±2.31</td>
<td>19.01 (18.79)</td>
<td>2.98 (2.68)</td>
</tr>
<tr>
<td>IRMOF-3-GL</td>
<td>Zn$<em>4$C$</em>{28}$H$<em>{42}$N$<em>2$O$</em>{19}$ = [Zn$<em>4$(C$</em>{10}$H$</em>{22}$N$<em>8$O$</em>{19}$)$_2$,2(C$_6$H$_5$)$_2$N]</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>35.12 (34.88)</td>
<td>2.21 (2.00)</td>
</tr>
<tr>
<td>IRMOF-3-GL-R</td>
<td>Zn$<em>4$C$</em>{28}$H$<em>{42}$N$<em>2$O$</em>{19}$ = [Zn$<em>4$(C$</em>{10}$H$</em>{22}$N$<em>8$O$</em>{19}$)$_2$,2(C$_6$H$_5$)$_2$N]</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>36.52 (36.20)</td>
<td>2.11 (2.08)</td>
</tr>
<tr>
<td>Nd-IRMOF-3-GL</td>
<td>Zn$<em>4$C$</em>{55}$H$_{55}$Cl$<em>2$N$<em>2$O$</em>{19}$ = [Zn$<em>4$(C$</em>{10}$H$</em>{22}$N$<em>8$O$</em>{19}$)$_2$,2(C$_6$H$_5$)$_2$N]</td>
<td>47.03 ±2.19</td>
<td>26.47 ±1.66</td>
<td>-</td>
<td>26.50 ±2.35</td>
<td>34.56 (34.44)</td>
<td>2.92 (2.89)</td>
</tr>
<tr>
<td>Eu-IRMOF-3-GL</td>
<td>Zn$<em>4$C$</em>{55}$H$_{55}$Cl$<em>2$N$<em>2$O$</em>{19}$ = [Zn$<em>4$(C$</em>{10}$H$</em>{22}$N$<em>8$O$</em>{19}$)$_2$,2(C$_6$H$_5$)$_2$N]</td>
<td>47.53 ±3.15</td>
<td>26.20 ±1.66</td>
<td>26.27 ±1.05</td>
<td>34.20 (34.13)</td>
<td>2.91 (2.86)</td>
<td>11.88 (11.83)</td>
</tr>
</tbody>
</table>

*the percentage calculated from ICP analysis (repeated 3 times) and EDS and the results are expressed as mean ±SD for determination of 10 crystals. C, H, N percentages were measured for 3 samples and calculated value between brackets.
Table S2. Elemental analysis of IRMOF-3-EM, IRMOF-3-MVK, Ln-IRMOF-3-EM and Ln-IRMOF-3-MVK (Ln = Nd, Eu) (%).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Metal &amp; chloride ratio*</th>
<th>S</th>
<th>C</th>
<th>H</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Zn</td>
<td>Nd</td>
<td>Eu</td>
<td>Cl</td>
<td></td>
</tr>
<tr>
<td>IRMOF-3-EM</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Zn₄C₄₀H₅₀N₆O₂₂Cl₂ =</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Zn₄O(C₆H₃NO₃)₂(C₆H₃NO₂)₀]₀</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nd-IRMOF-3-EM</td>
<td>29.44</td>
<td>17.64</td>
<td>-</td>
<td>52.92</td>
<td>12.02</td>
</tr>
<tr>
<td>Zn₄C₄₀H₅₀N₆O₂₂Cl₂S₄Nd</td>
<td>2.35</td>
<td>±1.12</td>
<td>-</td>
<td>±4.55</td>
<td>(11.96)</td>
</tr>
<tr>
<td>NdCl₂(C₆H₃NO₂)₀</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Eu-IRMOF-3-EM</td>
<td>28.99</td>
<td>17.99</td>
<td>-</td>
<td>53.02</td>
<td>11.89</td>
</tr>
<tr>
<td>Zn₄C₄₀H₅₀N₆O₂₂Cl₂S₄Eu</td>
<td>3.55</td>
<td>±1.13</td>
<td>-</td>
<td>±4.15</td>
<td>(11.87)</td>
</tr>
<tr>
<td>EuCl₂(C₆H₃NO₂)₀</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IRMOF-3-MVK</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Zn₄C₅₃H₁₈N₄O₁₅NdCl₂</td>
<td>36.88</td>
<td>21.08</td>
<td>-</td>
<td>42.04</td>
<td>15.65</td>
</tr>
<tr>
<td>NdC₆₅H₃₈O₁₈</td>
<td>3.21</td>
<td>±1.18</td>
<td>-</td>
<td>±2.05</td>
<td>(15.53)</td>
</tr>
<tr>
<td>Eu-IRMOF-3-MVK</td>
<td>37.05</td>
<td>19.93</td>
<td>-</td>
<td>43.02</td>
<td>15.31</td>
</tr>
<tr>
<td>Zn₄C₅₅H₄₆N₄O₂₂EuCl₂</td>
<td>3.19</td>
<td>±1.10</td>
<td>-</td>
<td>±2.19</td>
<td>(15.42)</td>
</tr>
<tr>
<td>EuCl₂(C₆H₃NO₂)₀</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*the percentage calculated from ICP analysis (repeated 3 times) and EDS and the results are expressed as mean ±SD for determination of 10 crystals. C, H, N percentages were measured for 3 samples and calculated value between brackets.

![Scheme S1. Reductive amination mechanism using sodium triacetoxyborohydride](image-url)
2. X-Ray diffraction

![Graph showing X-ray diffraction patterns](image)

**Fig. S1.** Powder X-ray diffraction patterns of (a) IRMOF-3, (b) IRMOF-3-GL, (c) Nd-IRMOF-3-GL and (d) Eu-IRMOF-3-GL.

![Graph showing X-ray diffraction patterns](image)

**Fig. S2.** Powder X-ray diffraction patterns of (a) IRMOF-3; (b) IRMOF-3-CA; (c) Nd-IRMOF-3-CA and (d) Eu-IRMOF-3-CA.
Fig. S3. Powder X-ray diffraction patterns of (a) IRMOF-3, (b) IRMOF-3-MVK, (c) Nd-IRMOF-3-MVK, (d) Eu-IRMOF-3-MVK.

Fig. S4. Powder X-ray diffraction patterns of (a) IRMOF-3, (b) IRMOF-3-EM, (c) Nd-IRMOF-3-EM, (d) Eu-IRMOF-3-EM.
3. NMR analysis

**Fig. S5.** $^1$H NMR spectrum of IRMOF-3.

**Fig. S6.** $^1$H NMR spectrum of IRMOF-3-CA, *= triethylamine
Fig. S7. Aromatic region of the $^1$H NMR of spectrum IRMOF-3-CA.

Fig. S8. $^{13}$C NMR spectrum of IRMOF-3-CA, *triethylamine.
Fig. S9. Solid-state $^{13}$C CP/MAS NMR spectrum of IRMOF-3-CA, *triethylamine.

Fig. S10. $^1$H NMR spectrum of IRMOF-3-Gl.
**Fig. S11.** Aromatic region of the $^1$H NMR spectrum of IRMOF-3-Gl. * Unmodified IRMOF-3.

**Fig. S12.** $^{13}$C NMR spectrum of IRMOF-3-GL.
Fig. S13. Solid-state $^{13}$C CP/MAS NMR spectrum of IRMOF-3-Gl.

Fig. S14. $^1$H NMR spectrum of IRMOF-3-Gl-R.
Fig. S15. Aromatic region of the $^1$H NMR spectrum of IRMOF-3-Gl-R. * Unmodified IRMOF-3.
Fig. S16. $^1$H NMR spectrum of IRMOF-3-EM.

Fig. S17. Aliphatic region of the $^1$H NMR spectrum of IRMOF-3-EM.
Fig. S18. Aromatic region of the $^1$H NMR spectrum of IRMOF-3-EM. * Unmodified IRMOF-3.

Fig. S19. $^{13}$C NMR spectrum of IRMOF-3-EM.
Fig. S20. HMBC spectrum of IRMOF-3-EM.

Fig. S21. Expansion of HMBC spectrum of IRMOF-3-EM.

Fig. S22. Expansion of HMBC spectrum of IRMOF-3-EM.
Fig. S23. Expansion of HSQC spectrum of IRMOF-3-EM.
Fig. S24. Expansion of HSQC spectrum of IRMOF-3-EM.

Fig. S25. $^1$H NMR spectrum of IRMOF-3-MVK.
**Fig. S26.** Expansion of the aromatic region of the $^1$H NMR spectrum of IRMOF-3-MVK. *Unmodified IRMOF-3.*

**Fig. S27.** Expansion of the aromatic region of the $^1$H NMR spectrum of IRMOF-3-MVK. *Unmodified IRMOF-3.*
**Fig. S28.** Aliphatic region of the $^1$H NMR spectrum of IRMOF-3-MVK. ? = oligomers of MVK.

**Fig. S29.** $^{13}$C NMR spectrum of IRMOF-3-MVK. ? = oligomers of MVK. * Unmodified IRMOF-3.
**Fig. S30.** HSQC spectrum of IRMOF-3-MVK

**Fig. S31.** Expansion of the HSQC spectrum of IRMOF-3-MVK.
Fig. S32. Expansion of the HSQC spectrum of IRMOF-3-MVK.

Fig. S33. HMBC spectrum of IRMOF-3-MVK.
Fig. S34. Expansion of the HMBC spectrum of IRMOF-3-MVK.

Fig. S35. Expansion of the HMBC spectrum of IRMOF-3-MVK.
Fig. S36. Expansion of the HMBC spectrum of IRMOF-3-MVK.

Fig. S37. 2D COSY spectrum of IRMOF-3-MVK.
Fig. S38. Expansion of the 2D COSY spectrum of IRMOF-3-MVK.
**Fig. S39.** Expansion of the 2D COSY spectrum of IRMOF-3-MVK.
4. FT-IR analysis

Fig. S40. FTIR spectra of (1) IRMOF-3-CA, (2) IRMOF-3-CA-Nd and (3) IRMOF-3-CA-Eu.
Fig. S41 FTIR spectra of (1) IRMOF-3-GL, (2) Nd-IRMOF-3-GL and (3) Eu-IRMOF-3-GL.
Fig. S42. FTIR spectra of IRMOF-3-MVK (black), Eu-IRMOF-3-MVK (red), and Nd-IRMOF-3-MVK (blue).
**Fig. S43.** FTIR spectra of IRMOF-3-EM (black), Eu-IRMOF-3-EM (red), and Nd-IRMOF-3-EM (blue).
5. Scanning Electron Microscopy

**Fig. S44.** SEM of: (a) Nd-IRMOF-3-CA, (c) Nd-IRMOF-3-GL, and optical microscopy photographs of (b) Nd-IRMOF-3-CA, (d) Nd-IRMOF-3-GL.

**Fig. S45.** SEM of: (a) Eu-IRMOF-3-CA, (c) Eu-IRMOF-3-GL, and optical microscopy photographs of (b) Eu-IRMOF-3-CA, (d) Eu-IRMOF-3-GL.
Fig. S46. SEM of: (a) Nd-IRMOF-3-MVK, (c) Nd-IRMOF-3-EM, and optical microscopy photographs of (b) Nd-IRMOF-3-MVK, (d) Nd-IRMOF-3-EM.

Fig. S47. SEM of: (a) Eu-IRMOF-3-MVK, (c) Eu-IRMOF-3-EM, and optical microscopy photographs of (b) Eu-IRMOF-3-MVK, (d) Eu-IRMOF-3-EM.
6. Photoluminescence spectroscopy

Fig. S48. Room-temperature (300 K) [left] emission spectra of IRMOF-3 (black) at 280 nm, IRMOF-3-GL (blue) at 280 nm, IRMOF-3-CA (red) at 280 nm, IRMOF-3-MVK (purple) at 421 nm and IRMOF-3-EM (green) at 385 nm; [right] excitation spectra of IRMOF-3 (black) at 450 nm, IRMOF-3-GL (blue) at 475 nm, IRMOF-3-CA (red) at 460 nm, IRMOF-3-MVK (purple) at 471 nm and IRMOF-3-EM (green) at 545 nm.

Fig. S49. Room temperature (300K) (left) emission at 370 nm and (right) excitation at 615 nm spectra of Eu-IRMOF-3-CA.
Fig. S50. High-resolution emission spectra (300K) of Eu-IRMOF-3-GL (left) excited at 430 nm and Eu-IRMOF-3-EM (right) excited at 375 nm.
Fig. S51. Room temperature emission decay curves of (a) Nd-IRMOF-3-GL, (b) Nd-IRMOF-3-MVK and (c) Nd-IRMOF-3-CA monitored around 1064 nm and excited at (a, c) 365 nm and (b) 395 nm. The solid lines represent the data best fit (R > 0.98) to a single exponential function. The insets show the fit residual plot.
**Fig. S52.** Room-temperature emission decay curves of (a) Eu-IRMOF-3-GL, (b) Eu-IRMOF-3-MVK (355 nm), (b) Eu-IRMOF-3-CA and (d) Eu-IRMOF-3-EM monitored around 616 nm and excited at (a) 420 nm, (b, d) 355 nm, and (d) 380 nm. The solid lines represent the data best fit (R>0.98) to a single exponential function. The insets show the fit residual plot.