SUPPLEMENTARY INFORMATION

Near-Infrared Emitters Based on Post-Synthetic Modified Ln^{3+}-IRMOF-3

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Material and methods

1. Materials

2-Aminoterephthalic acid (99%, Aldrich), zinc nitrate hexahydrate (Merck), *N*,*N*-dimethylformamide (99.9%, Aldrich), chloroform (99.5%, Aldrich), toluene (PA, Fisher Scientific), neodymium chloride ($NdCl_3.6H_2O$) (99%, Aldrich) ,Yttrium(III) chloride ($YCl_3.6H_2O$) (99%, Aldrich).

2. Synthesis of IRMOF-3

$Zn(NO_3)_2.6H_2O$ (1.795 g, 6 mmol) and 2-aminoterephthalic acid (0.37 g, 2 mmol) were dissolved in *N*,*N*-dimethylformamide (DMF, 50 mL) at room temperature. The obtained solution was sealed and placed in the oven at 100°C for 18 h. The obtained crystals were separated, washed with DMF (three times), chloroform (three times), then immersed into chloroform over night to remove DMF guest molecules from IRMOF-3, and finally stored under chloroform.

3. Post-synthetic modification of IRMOF-3

3.1. Synthesis of IRMOF-3-AC

A toluene solution of pentane-2,4-dione (0.6 mL, 6 mmol) was added dropwise at room temperature to IRMOF-3 (1.0 g, 3.3 mmol equiv of $–NH_2$) dispersed in toluene (15 mL), being the resulting mixture sealed and kept for 1 day at 60°C. The crystals were then washed with fresh toluene three times and finally stored under toluene. CHN analysis for $[Zn_4O(C_{13}H_{11}NO_5)_{1.38}(C_8H_5NO_4)_{1.62}]$: Expected: C 39.98%, H 2.53%, N 4.53%. Found: C 41.30%, H 2.81%, N 4.63%. FTIR (KBr pellet, cm^{-1}): 3440 (br), 3336 (br), 2913 (w),1620 (sh), 1578 (sh), 1496 (w), 1438 (s), 1384 (s), 1262 (s), 1106 (w), 1026 (w), 944 (m), 896 (w), 838 (m), 770 (s), 698 (w), 588 (m), 516 (w).

3.2. Synthesis of IRMOF-3-OL

A $CHCl_3$ solution (15 mL) of 3-(2-hydroxyphenyl)-3-oxopropanal (656 mg, 4 mmol) was added dropwise at room temperature to IRMOF-3 (1.0 g, 3.3 mmol equiv of $–NH_2$) dispersed in $CHCl_3$ (15 mL), being the mixture refluxed for 2 days. The crystals were then washed with fresh $CHCl_3$ three times and finally stored under $CHCl_3$. CHN analysis for $[Zn_4O(C_{17}H_{11}NO_6)_{2.7}(C_8H_5NO_4)_{0.3}]$: Expected: C 47.96%, H 2.60%, N 3.47%. Found: C 48.03%, H 2.71%, N 3.56%. FTIR (KBr pellet, cm^{-1}): 3400 (br), 3222 (br), 3058 (br), 2933 (w),1660 (w), 1612 (sh), 1578 (sh), 1513 (w), 1488 (w), 1427 (s), 1378 (s), 1288 (sh), 1214 (br), 1159 (br), 1120 (w), 1026 (s), 973 (m), 890 (s), 838 (m), 798 (s), 763 (sh), 701 (w), 674 (s), 617 (w), 559 (m), 516 (w), 460 (br), 372 (w). ^1H NMR (300 MHz, d_6-DMSO, dilute DCl): δ 6.30 (d, 1H, *J* 8.3 Hz, H-i), 6.89-6.93 (m, 2H, H-p and H-n), 7.45 (dt, *J* 7.7 and 1.4 Hz, H-o), 7.65 (dd, 1H, *J* 8.17 and 1.4 Hz, H-m), 7.94 (dd, 1H, *J* 8.6 and 1.0 Hz, H-d), 8.01 (d, 1H, *J* 8.6 Hz, H-c), 8.083 (d, 1H, *J* 8.3 Hz, H-j) 8.085 (d, 1H, *J* 1.0 Hz, H-g), (resonances of the modified MOF; see numbering in Fig. S4-S6).

4. Complexation with lanthanides

4.1. Synthesis of Nd-IRMOF-3-AC

A DMSO (15 mL) solution of $NdCl_3.6H_2O$ (250 mg, 1 mmol) was added dropwise at room temperature to IRMOF-3-AC (340 mg, 1 mmol) dispersed in toluene (15 mL), being the resulting mixture stand for 3 days. The sample was washed twice with toluene and dried in air. CHN analysis for $[Zn_4O(C_{27}H_{52}NO_{12}S_7Nd)_{1.38}(C_8H_5NO_4)_{1.62}]$: Expected: C 32.07%, H 4.28%, N 2.23%, S 16.47%. Found: C 33.04%, H 5.01%, N 2.50%, S 17.21%. FTIR (KBr pellet, cm^{-1}): 3440 (w), 3336 (w), 3000 (w), 2965 (w), 2913 (w), 1627 (sh), 1578 (sh), 1496 (w), 1438 (s), 1384 (s), 1330 (w), 1262 (s), 1106 (w), 1091 (m), 1026 (sh), 944 (m), 896 (w), 800 (s), 770 (s), 698 (m), 588 (m), 568 (w), 516 (w), 406 (m), 350 (m).

4.2. Synthesis of Nd-IRMOF-3-OL

An ethanolic solution (15 mL) of $NdCl_3.6H_2O$ (250 mg, 1 mmol) was added dropwise at room temperature to IRMOF-3-OL (420 mg, 1 mmol) dispersed in $CHCl_3$ (15 mL), being the resulting mixture stand for 3 days at room temperature. The sample was washed twice with $CHCl_3$ then washed with ethanol 3 times and dried in air. CHN analysis for $[Zn_4O(C_{17}H_9NO_6)_{2.7}Nd_{0.9}(C_8H_5NO_4)_{0.3}]$: Expected: C 43.49%, H 1.95%, N 3.15%. Found: C 43.85%, H 2.10%; N 3.34%. FTIR (KBr pellet, cm^{-1}): 3435 (w), 3205 (w), 2920 (w), 1614 (w), 1569 (sh), 1514 (w), 1486 (m), 1427 (s), 1384 (sh), 1282 (sh), 1209 (s), 1157 (m), 1118 (m), 1085 (w), 1029 (s), 973 (s), 946 (m), 890 (m), 842 (s), 802 (s), 770 (s), 700 (m), 674 (s), 632 (w), 568 (br), 516 (br), 422 (w), 360 (br).

4.3. Synthesis of Nd-Y-IRMOF-3-OL

An ethanolic solution (15 mL) of $NdCl_3.6H_2O$ (12.5 mg, 0.05 mmol) and YCl_3 (185.25 mg, 0.95 mmol) was dropwise added at room temperature to IRMOF-3-OL (420 mg, 1 mmol) dispersed in $CHCl_3$ (15 mL), being the resulting mixture stand for 3 days at room temperature. The sample was washed twice with $CHCl_3$ then washed with ethanol 3 times and dried in air. CHN analysis for $[Zn_4O(C_{17}H_9NO_6)_{2.7}Nd_{0.05}Y_{0.85}(C_8H_5NO_4)_{0.3}]$: Expected: C 45.08%, H 2.02%, N 3.27%. Found: C 45.68%, H 2.12%, N 3.35%. FTIR (KBr pellet, cm^{-1}): 3432 (w), 3201 (w), 2919 (w), 1614 (w), 1569 (sh), 1514 (w), 1486 (m), 1427 (s), 1384 (sh), 1282 (sh), 1209 (s), 1157 (m), 1118 (m), 1085 (w), 1029 (s), 973 (s), 946 (m), 890 (m), 842 (s), 819 (w), 802 (s), 770 (s), 700 (m), 674 (s), 632 (w), 568 (br), 516 (br), 422 (w), 360 (br).

5. Characterization

The powder diffraction X-ray (XRD) data were collected on an X'Pert MPD Philips diffractometer (Cu Kα X-radiation at 40 kV and 50 mA). EDS measurements were carried out on a SEM using a Hitachi SU-70 with a field emission gun. The optical microscope examinations were carried out with Leica EZ4HD Digital Microscope-3.0 Megapixel. Fourier transform infrared spectroscopy (FT-IR, Mattson 5000) was carried out in the range of 4000-350 cm^{-1} in transmission mode. The pellets were prepared by adding 1-2 mg of the MOFs to 200 mg of KBr. The mixture was then carefully mixed and compressed at a pressure of 10 kPa in order to form transparent pellets. CNH contents were determined by LECO CHNS-932 element analyzer. Solution NMR were recorded on Bruker Avance 300 spectrometer (300 MHz for ^{1}H NMR) using a solution prepared by digesting 7 mg of sample in mixture of d_6-DMSO (500 µL) and dilute DCl (100 µL, 35% DCl). All ^{13}C CP/MAS spectra were recorded on a Bruker AVANCE-400 (DRX) NMR spectrometer operating at 100 MHz for carbon, using 7 mm CP/MAS Bruker double-bearing probes. All samples were finely ground before packing in the rotors. Rotors were spun at rates 9 kHz and the ^{13}C CP/MAS spectra were recorded using a proton 90° pulse length of 4.0 µs, 1 ms contact time and recycle time of 20 s. The photoluminescence spectra in the visible and NIR spectral ranges were recorded at room temperature with a modular double grating excitation spectrofluorimeter with a TRIAX 320 emission monochromator (Fluorolog-3, Horiba Scientific) coupled to a R928 and H9170 Hamamatsu photomultipliers, respectively, using a front face acquisition mode. The excitation source was a 450 W Xe arc lamp. The emission spectra were corrected for detection and optical spectral response of the spectrofluorimeter and the excitation spectra were corrected for the spectral distribution of the lamp intensity using a photodiode reference detector.

Table S1. Elemental analysis of IRMOF-3-AC, IRMOF-3-OL, Nd-IRMOF-3-AC, Nd-IRMOF-3-OL and Nd-Y-IRMOF-3-OL (%).

<table>
<tr><th>Sample</th><th>Zn*</th><th>Nd*</th><th>S</th><th>C</th><th>H</th><th>N</th></tr>
<tr><td>IRMOF-3-AC
$[Zn_4C_{30.9}H_{23.28}N_3O_{14.38}]=[Zn_4O(C_{13}H_{11}NO_5)_{1.38}(C_8H_5NO_4)_{1.62}]$</td><td>100</td><td>-</td><td>-</td><td>41.30
(39.98)</td><td>2.81
(2.53)</td><td>4.63
(4.53)</td></tr>
<tr><td>Nd-IRMOF-3-AC
$[Zn_4C_{50.22}H_{79.86}N_3Nd_{1.38}O_{24.04}S_{9.66}]=[Zn_4O(C_{27}H_{52}NO_{12}S_7Nd)_{1.38}(C_8H_5NO_4)_{1.62}]$</td><td>74.34
±1.61</td><td>25.65
±2.16</td><td>17.21
(16.47)</td><td>33.04
(32.07)</td><td>5.01
(4.28)</td><td>2.50
(2.23)</td></tr>
<tr><td>IRMOF-3-OL
$[Zn_4C_{48.3}H_{31.2}N_3O_{18.4}]=[Zn_4O(C_{17}H_{11}NO_6)_{2.7}(C_8H_5NO_4)_{0.3}]$</td><td>100</td><td>-</td><td>-</td><td>48.03
(47.96)</td><td>2.71
(2.60)</td><td>3.56
(3.47)</td></tr>
<tr><td>Nd-IRMOF-3-OL
$[Zn_4C_{48.3}H_{25.8}N_3Nd_{0.9}O_{18.4}]=[Zn_4O(C_{17}H_9NO_6)_{2.7}Nd_{0.9}(C_8H_5NO_4)_{0.3}]$</td><td>81.63
±2.13</td><td>18.36
±1.12</td><td>-</td><td>43.85
(43.49)</td><td>2.10
(1.95)</td><td>3.34
(3.15)</td></tr>
<tr><td rowspan="3">Nd-Y-IRMOF-3-OL
$[Zn_4C_{48.3}H_{25.8}N_3Nd_{0.05}Y_{0.85}O_{18.4}]=[Zn_4O(C_{17}H_9NO_6)_{2.7}Nd_{0.05}Y_{0.85}(C_8H_5NO_4)_{0.3}]$</td><td colspan="3">Control metal adding</td><td rowspan="3">45.68
(45.08)</td><td rowspan="3">2.12
(2.02)</td><td rowspan="3">3.35
(3.27)</td></tr>
<tr><td>Zn*</td><td>Nd*</td><td>Y*</td></tr>
<tr><td>81.64
±2.13</td><td>1.02
±0.50</td><td>17.34
±1.12</td></tr>
</table>

*The percentage calculated from 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.

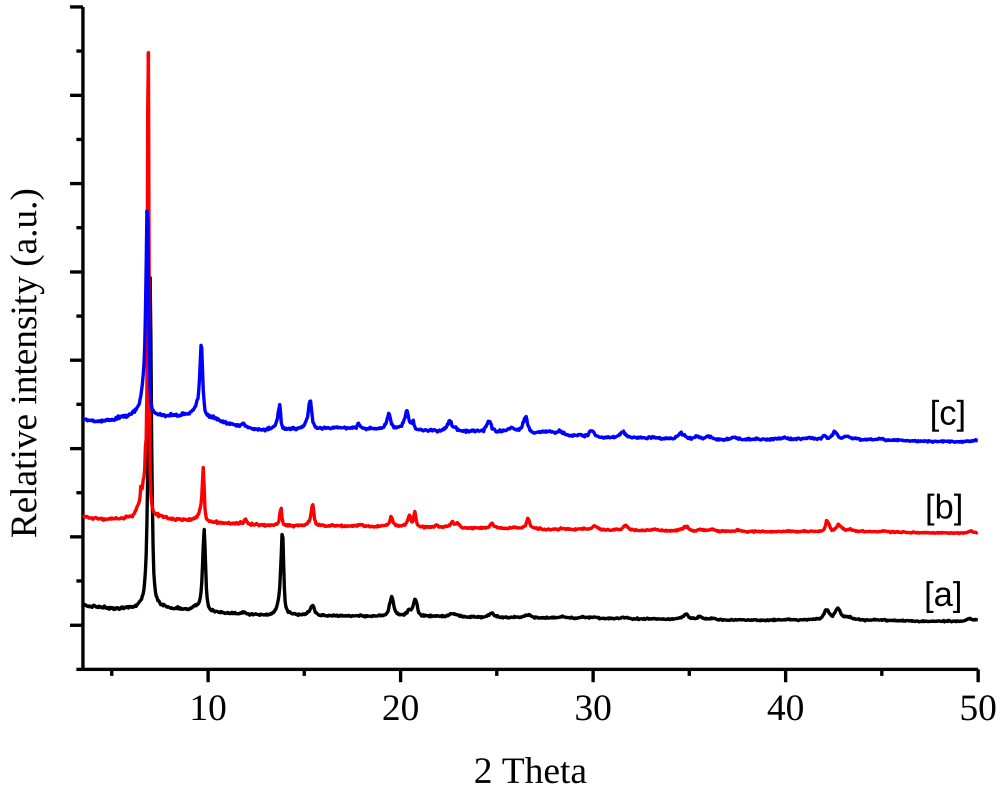

Fig. S1. Powder XRD of (a) IRMOF-3, (b) IRMOF-3-OL and (c) IRMOF-3-AC

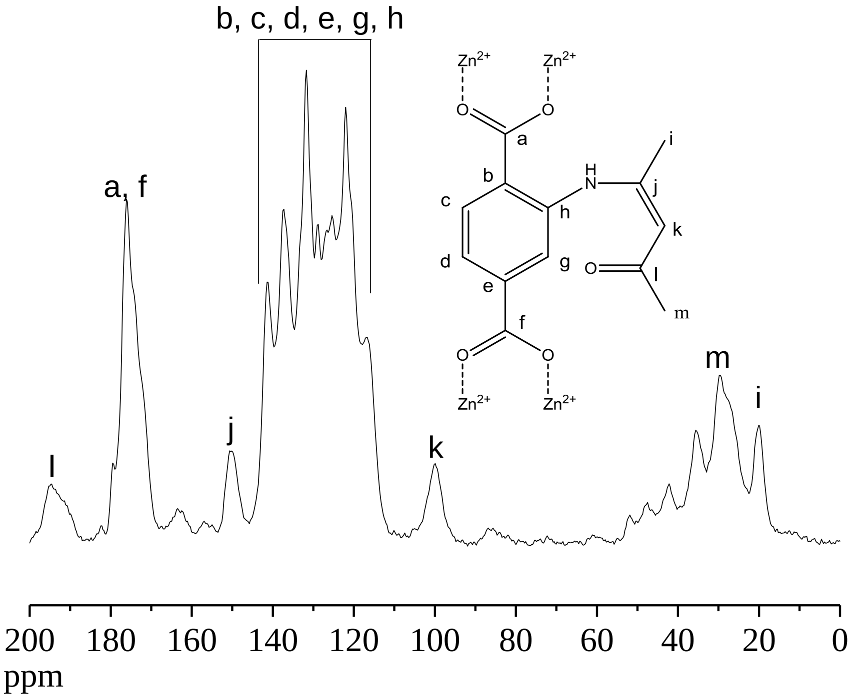

Fig. S2. Solid-state ^{13}C CP/MAS NMR spectrum of IRMOF-3-AC.

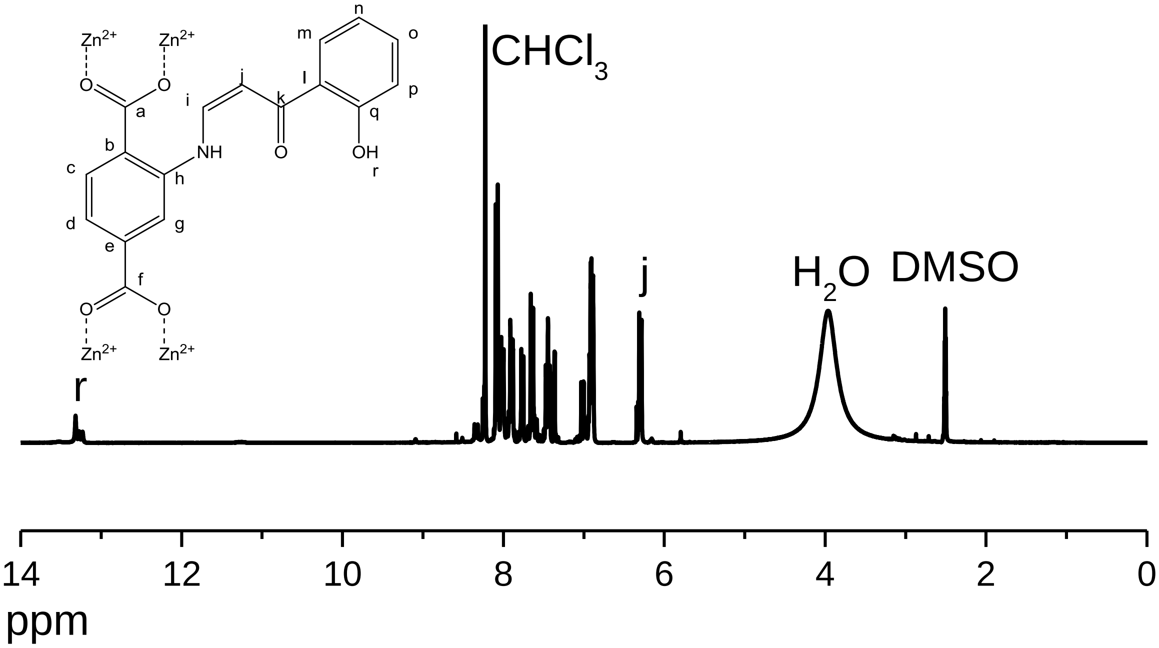

Fig. S3. Solution ^{1}H NMR spectrum of acid-digested IRMOF-3-OL.

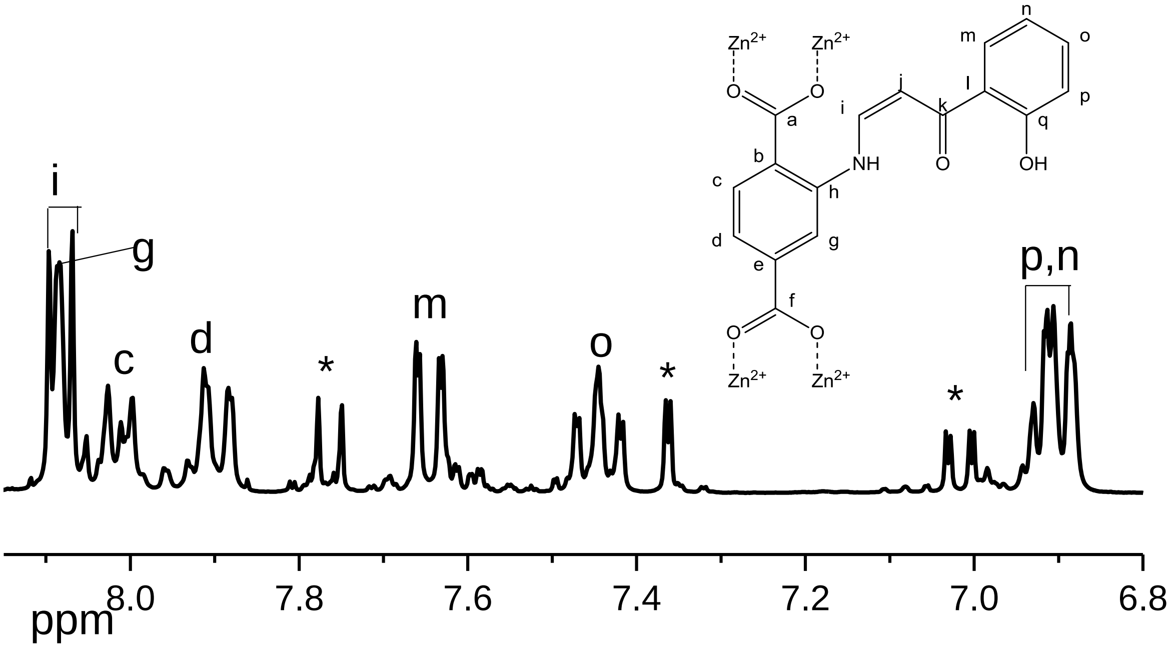

Fig. S4. Solution ^{1}H NMR spectrum of acid-digested IRMOF-3-OL (expansion), *unmodified MOF.

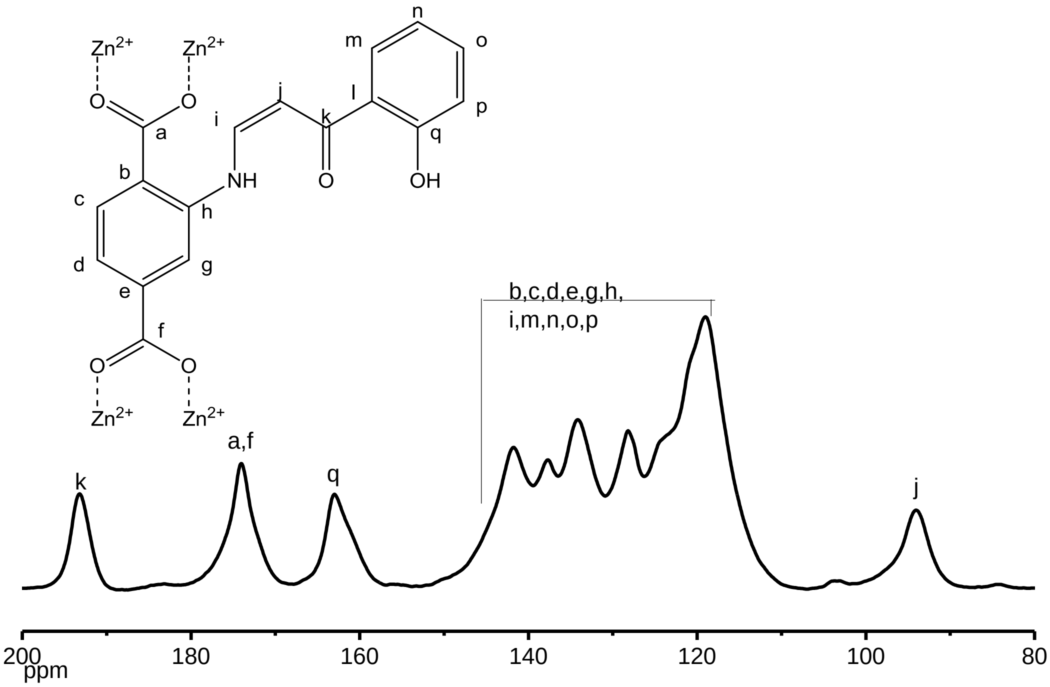

Fig. S5. Solid-state ^{13}C CP/MAS NMR spectrum of IRMOF-3-OL

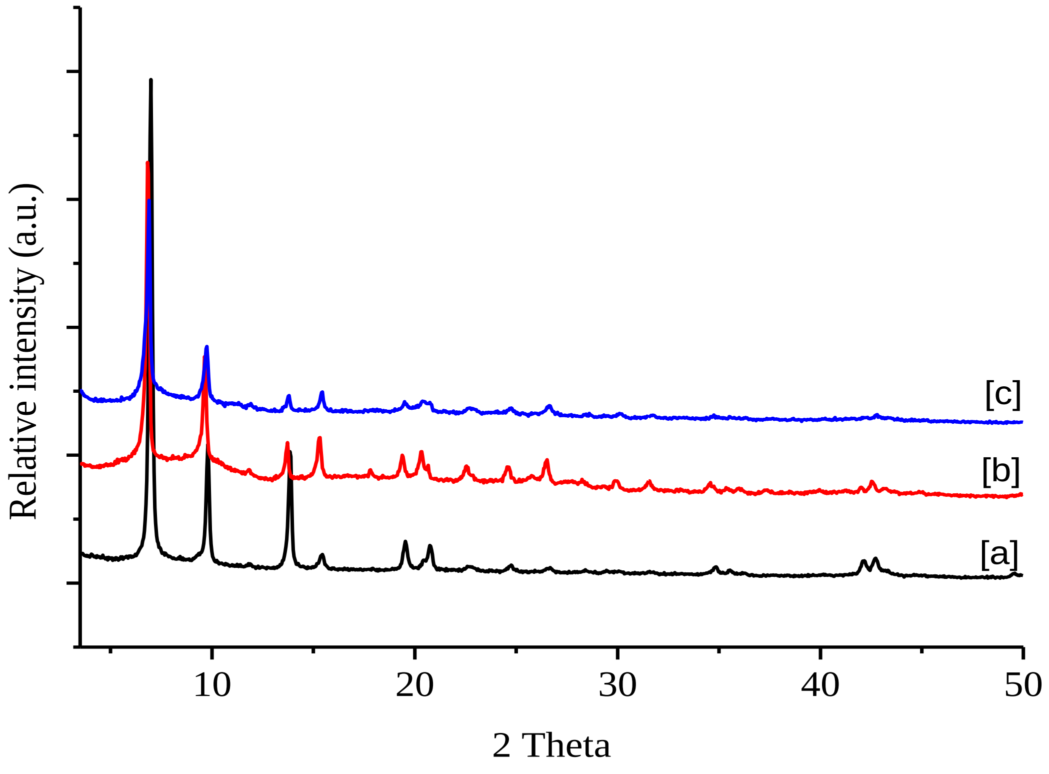

Fig. S6. Powder XRD of (a) IRMOF-3; (b) IRMOF-3-AC and (c) Nd-IRMOF-3-AC.

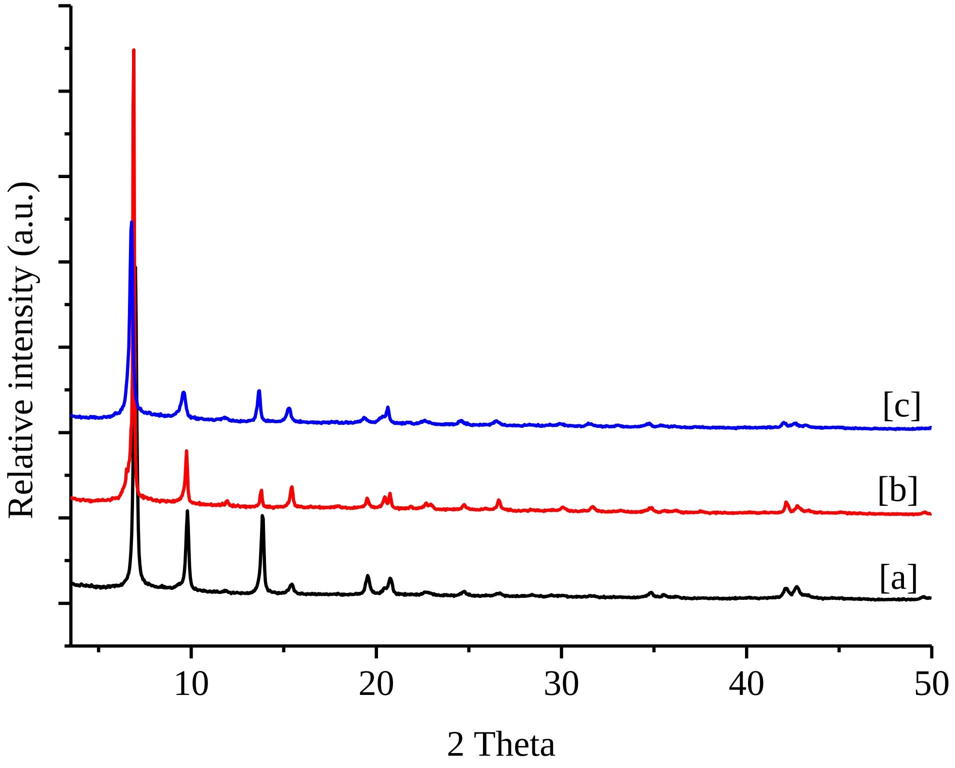

Fig. S7. Powder XRD of (a) IRMOF-3; (b) IRMOF-3-OL and (c) Nd-IRMOF-3-OL.

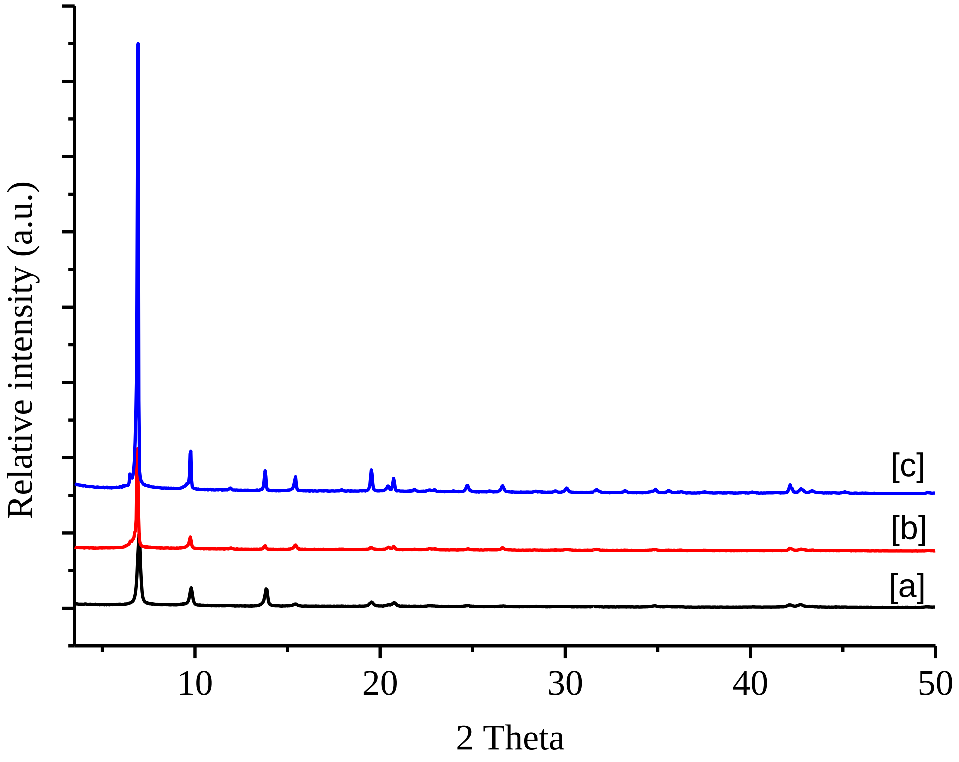

Fig. S8. Powder XRD of (a) IRMOF-3; (b) IRMOF-3-OL and (c) Nd-Y-IRMOF-3-OL.

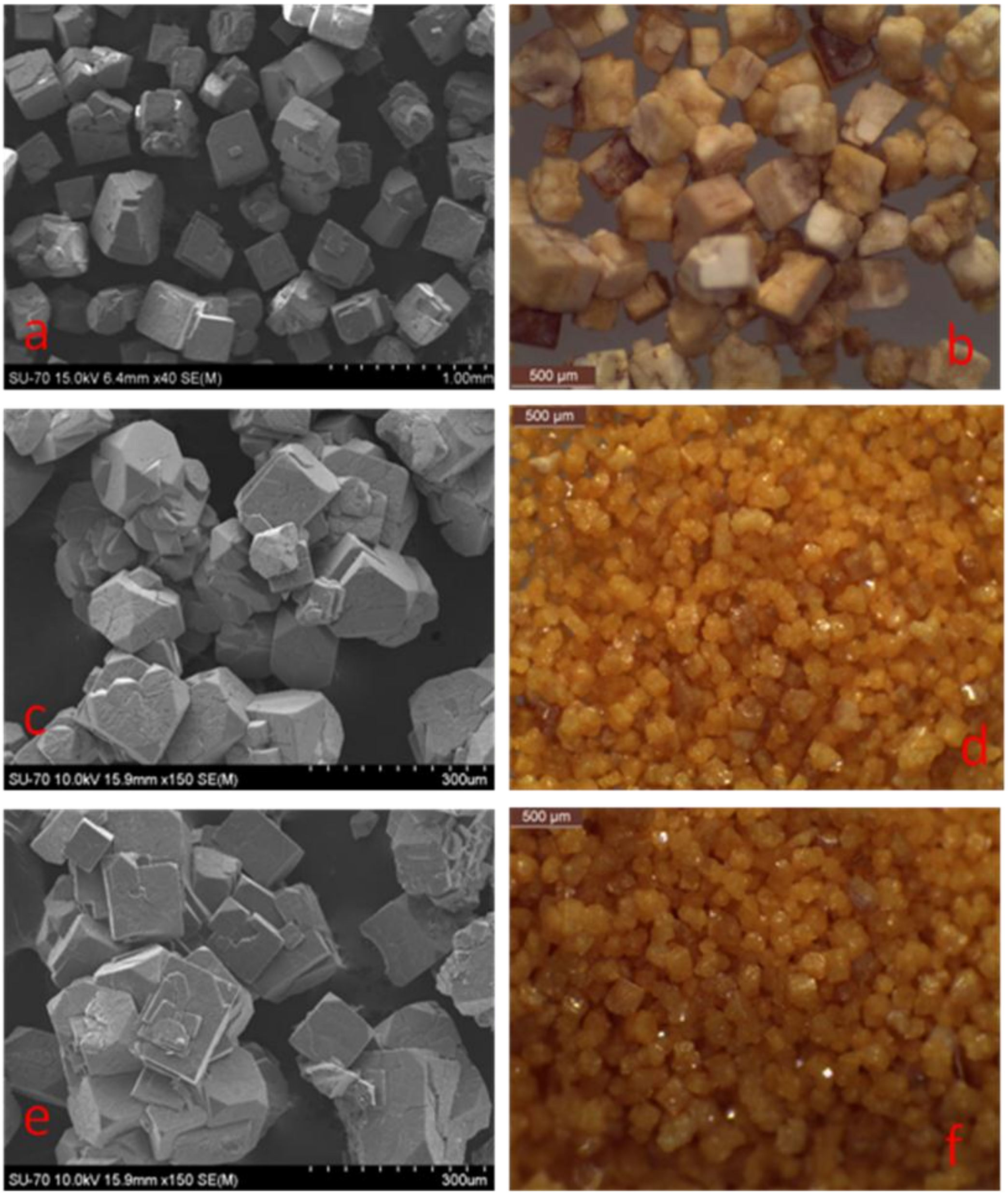

Fig. S9. SEM of: (a) Nd-IRMOF-3-AC, (c) Nd-IRMOF-3-OL, (e) Nd-Y-IRMOF-3-OL and optical microscopy photographs of (b) Nd-IRMOF-3-AC, (d) Nd-IRMOF-3-OL, (f) Nd-Y-IRMOF-3-OL.

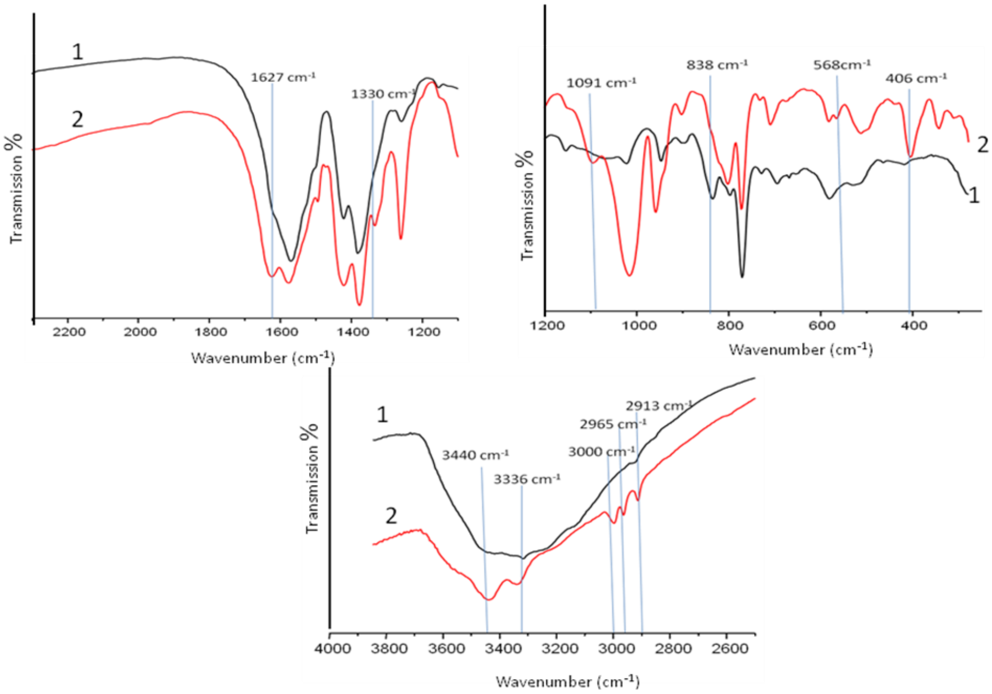

Fig. S10. FTIR spectra of (1) IRMOF-3-AC and (2) Nd-IRMOF-3-AC.

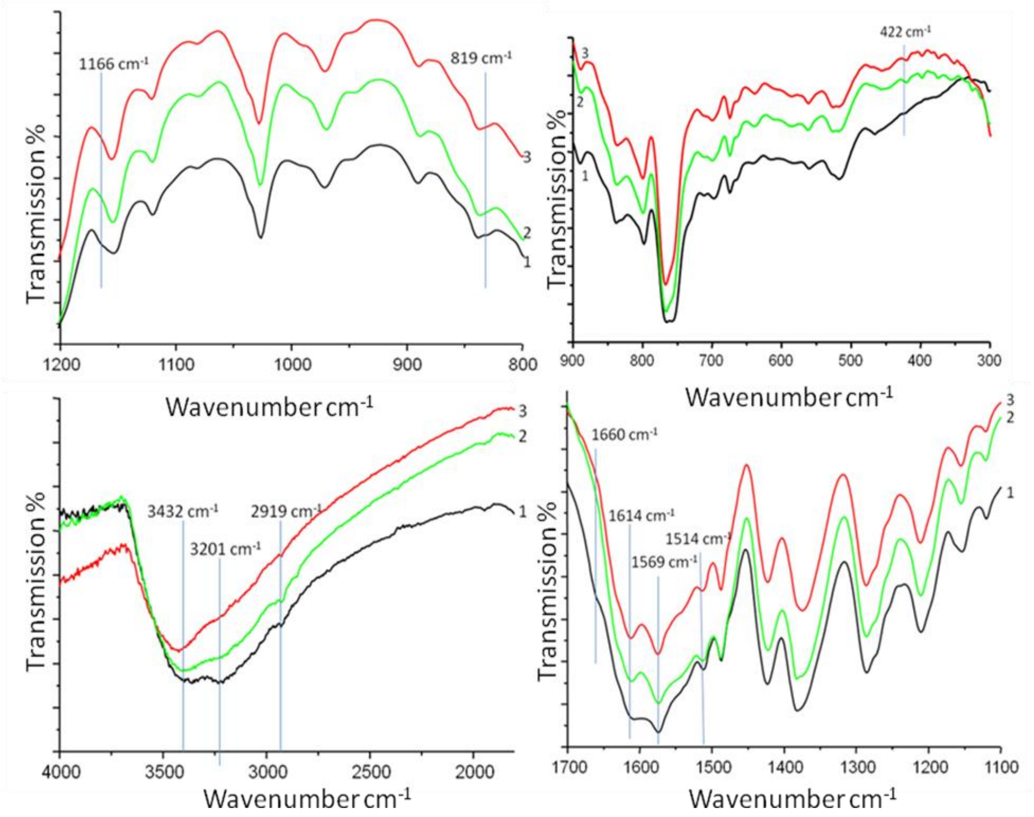

Fig. S11. FTIR spectra of (1) IRMOF-3-OL, (2) Nd-IRMOF-3-OL and (3) Nd-Y-IRMOF-3-OL.

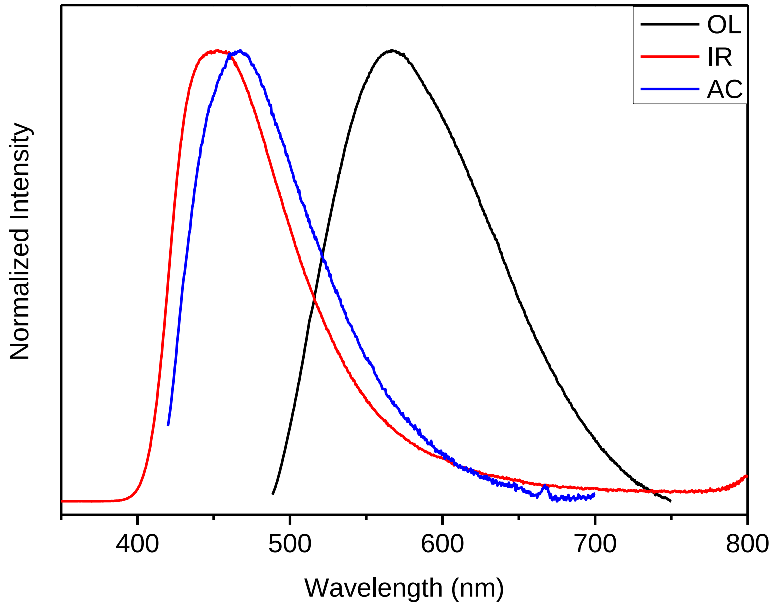

Fig. S12. Emission spectra of IRMOF-3 (IR) excited at 280 nm, IRMOF-3-AC (AC) excited at 405 nm, IRMOF-3-OL (OL) excited at 465 nm.

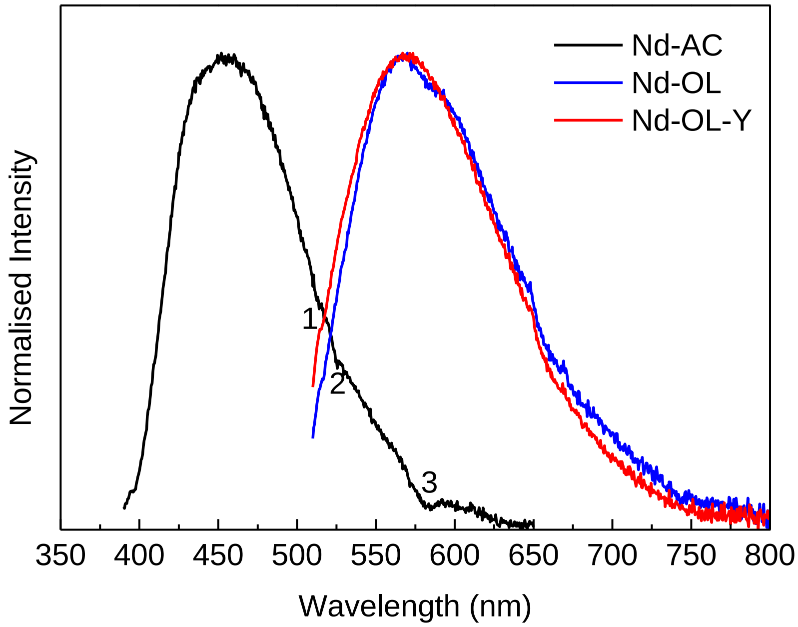

Fig. S13. Emission spectra of Nd-IRMOF-3-AC (Nd-AC), Nd-IRMOF-3-OL (Nd-OL) and Nd-Y-IRMOF-3-OL (Nd-Y-OL) MOFs excited at 370 nm (Nd-AC) and 490 nm (Nd-OL, Nd-Y-OL). The intra-4*f* ^{3} $^{4}I_{9/2}\rightarrow{}^{4}G_{7/2}$ (1), $^{4}I_{9/2}\rightarrow{}^{2}K_{13/2}$ (2), and $^{4}I_{9/2}\rightarrow{}^{2}G_{7/2}$ (3) self-absorptions are discerned.