Electronic Supplementary Information (ESI)

# Erbium(III)-Based Metal-Organic Frameworks with Tunable Upconversion Emissions

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## Experimental Section

### Materials and General Methods

All the chemicals for the Ln-MOFs synthesis were obtained commercially and used as received. Infrared spectra (IR) were measured on a TENSOR 27 OPUS (Bruker) using the KBr pellet in the range of 4000-400 $cm^{-1}$. Thermogravimetric analyses (TGA) were carried out on a Rigaku standard TG-DTA analyzer with a heating rate of 10 °C $min^{-1}$, and an empty $Al_2O_3$ crucible was used as reference. The room-temperature powder X-ray diffraction spectra (PXRD) were recorded on a Rigaku D/Max-2500 diffractometer at 40 kV, 100 mA with a Cu-target tube and a graphite monochromator. All the luminescence measurements were performed on a Horiba Jobin Yvon spectrometer (Nanolog FL3-2iHR). Simulation of the XRPD pattern was carried out by the single-crystal data and diffraction-crystal module of the Mercury (Hg) program available free of charge via the Internet at http://www.iucr.org.

### Synthesis of 1 (Y-MOF)

A mixture of $Y(NO_3)_3 \cdot 6H_2O$ (0.05 mmol), $H_4$bptc (biphenyl-2,5,2′,5′-tetracarboxylic acid, 0.030 mmol), $H_2$BDC (1,4-dicarboxybenzene, 0.0015 mmol) and 6 mL $H_2O/CH_3OH$ (v/v = 5:1) was added in a 10 mL stainless steel sealed Teflon vial and heated to 150 °C for 72 hours. The reaction vessel was cooled down to room temperature and yellow crystals were collected with ca 60% yield based on $H_4$bptc. The sample was dried at 60 °C overnight to remove the guest solvent molecules. Anal. Calcd for $C_{19}H_{10}Y_{1.5}O_{12}$: C, 53.02; H, 2.33. Found: C, 51.20; H, 2.11. FT-IR (KBr pellets, $cm^{-1}$): 3061 m, 1693 w, 1570 s, 1488 s, 1411 m, 1286 m, 1257 m, 1138 s, 1042 s, 915 s, 865 s, 776 s, 752 s, 528 s.

### Synthesis of 2 (Yb-MOF)

A mixture of $Yb(NO_3)_3 \cdot 5H_2O$ (0.050 mmol), $H_4$bptc (0.030 mmol), $H_2$BDC (0.0015 mmol) and 6 mL $H_2O/CH_3OH$ (v/v = 5:1) was added in a 10 mL stainless steel sealed Teflon vial and heated to 150 °C for 72 hours. The reaction vessel was cooled down to room temperature and yellow crystals were collected with ca 55% yield based on $H_4$bptc. The sample was dried at 60 °C overnight to remove the guest solvent molecules. Anal. Calcd for $C_{19}H_{10}Yb_{1.5}O_{12}$: C, 49.13; H, 2.16. Found: C, 49.42; H, 2.88. FT-IR (KBr pellets, $cm^{-1}$): 3439 m, 3060 m, 1691 w, 1570 s, 1488 s, 1411 m, 1257 m, 1138 s, 1042 s, 915 s, 865 s, 776 s, 752 s, 528 s.

**Synthesis of 3 (Er-MOF)**

A mixture of $Er(NO_3)_3 \cdot 6H_2O$ (0.050 mmol), $H_4$bptc (0.030 mmol), $H_2$BDC (0.0015 mmol) and 6 mL $H_2O/CH_3OH$ (v/v = 5:1) was added in a 10 mL stainless steel sealed Teflon vial and heated to 150 °C for 72 hours. The reaction vessel was cooled down to room temperature and pink crystals were collected with ca 58% yield based on $H_4$bptc. The sample was dried at 60 °C overnight to remove the guest solvent molecules at 60 °C. Anal. Calcd for $C_{19}H_{10}Er_{1.5}O_{12}$: C, 49.32; H, 2.17. Found: C, 51.50; H, 2.27. FT-IR (KBr pellets, $cm^{-1}$): 3440 m, 3061 m, 1693 w, 1570 s, 1488 s, 1411 m, 1286 m, 1257 m, 1138 s, 1042 s, 915 s, 865 s, 776 s, 752 s, 528 s.

**Synthesis of 4 (Y/Yb/Er = 0/95/5)**

A mixture of $Yb(NO_3)_3 \cdot 5H_2O$ (0.0475 mmol), $Er(NO_3)_3 \cdot 6H_2O$ (0.0025 mmol), $H_4$bptc (0.030 mmol), $H_2$BDC (0.0015 mmol) and 6 mL $H_2O/CH_3OH$ (v/v = 5:1) was added in a 10 mL stainless steel sealed Teflon vial and heated to 150 °C for 72 hours. The reaction vessel was cooled down to room temperature and yellow crystals were collected with ca 62% yield based on $H_4$bptc. The sample was dried at 60 °C overnight to remove the guest solvent molecules at 60 °C. Anal. Calcd for $C_{19}H_{10}Yb_{1.4}Er_{0.14}O_{12}$: C, 49.48; H, 2.17. Found: C, 50.34; H, 2.96. FT-IR (KBr pellets, $cm^{-1}$): 3440 m, 3061 m, 1693 w, 1488 s, 1411 m, 1286 m, 1257 m, 1137 s, 1042 s, 916 s, 866 s, 776 s, 752 s, 528 s.

**Synthesis of 5 (Y/Yb/Er = 0/70/30)**

A mixture of $Yb(NO_3)_3 \cdot 5H_2O$ (0.035 mmol), $Er(NO_3)_3 \cdot 6H_2O$ (0.015 mmol), $H_4$bptc (0.030 mmol), $H_2$BDC (0.0015 mmol) and 6 mL $H_2O/CH_3OH$ (v/v = 5:1) was added in a 10 mL stainless steel sealed Teflon vial and heated to 150 °C for 72 hours. The reaction vessel was cooled down to room temperature and yellow crystals were collected with ca 50% yield based on $H_4$bptc. The sample was dried at 60 °C overnight to remove the guest solvent molecules at 60 °C. Anal. Calcd for$C_{19}H_{10}Yb_{1.28}Er_{0.23}O_{12}$: C, 49.61; H, 2.20. Found: C, 49.43; H, 2.87. FT-IR (KBr pellets, $cm^{-1}$): 3441 s, 2986 s, 1690 w, 1569 s, 1488 s, 1410 m, 1286 s, 1257 m, 1137 s, 1042 s, 915 s, 865 s, 776 s, 752 s, 528 s.

**Synthesis of 6 (Y/Yb/Er = 0/50/50)**

A mixture of $Yb(NO_3)_3 \cdot 5H_2O$ (0.025 mmol), $Er(NO_3)_3 \cdot 6H_2O$ (0.025 mmol), $H_4$bptc (0.030 mmol), $H_2$BDC (0.0015 mmol) and 6 mL $H_2O/CH_3OH$ (v/v = 5:1) was added in a 10 mL stainless steel sealed Teflon vial and heated to 150 °C for 72 hours. The reaction vessel was

cooled down to room temperature and pink crystals were collected with ca 52% yield based on $H_4$bptc. The sample was dried at 60 °C overnight to remove the guest solvent molecules at 60 °C. Anal. Calcd for $C_{19}H_{10}Yb_{0.9}Er_{0.6}O_{12}$: C, 49.56; H, 2.24. Found: C, 51.47; H, 2.84. FT-IR (KBr pellets, $cm^{-1}$): 3432 m, 2986 m, 1690 w, 1568 s, 1488 m, 1410 m, 1286 m, 1257 m, 1137 s, 1042 s, 914 s, 865 s, 776 s, 752 s, 693 s, 528 s.

**Synthesis of 7 (Y/Yb/Er = 30/60/10)**

A mixture of $Y(NO_3)_3 \cdot 6H_2O$ (0.015 mmol), $Yb(NO_3)_3 \cdot 5H_2O$ (0.03 mmol), $Er(NO_3)_3 \cdot 6H_2O$ (0.005 mmol), $H_4$bptc (0.030 mmol), $H_2$BDC (0.0015 mmol) and 6 mL $H_2O/CH_3OH$ (v/v = 5:1) was added in a 10 mL stainless steel sealed Teflon vial and heated to 150 °C for 72 hours. The reaction vessel was cooled down to room temperature and yellow crystals were collected with ca 63% yield based on $H_4$bptc. The sample was dried at 60 °C overnight to remove the guest solvent molecules at 60 °C. Anal. Calcd for $C_{19}H_{10}Y_{0.45}Yb_{0.8}Er_{0.25}O_{12}$: C, 50.02; H, 2.34. Found: C, 49.87; H, 2.56. FT-IR (KBr pellets, $cm^{-1}$): 3061 m, 1693 w, 1570 s, 1488 s, 1411 m, 1286 m, 1257 m, 1138 s, 1042 s, 915 s, 865 s, 776 s, 752 s, 528 s.

**Synthesis of 8 (Y/Yb/Er = 30/50/20)**

A mixture of $Y(NO_3)_3 \cdot 6H_2O$ (0.015 mmol), $Yb(NO_3)_3 \cdot 5H_2O$ (0.025 mmol), $Er(NO_3)_3 \cdot 6H_2O$ (0.010 mmol), $H_4$bptc (0.030 mmol), $H_2$BDC (0.0015 mmol) and 6 mL $H_2O/CH_3OH$ (v/v = 5:1) was added in a 10 mL stainless steel sealed Teflon vial and heated to 150 °C for 72 hours. The reaction vessel was cooled down to room temperature and yellow crystals were collected with ca 48% yield based on $H_4$bptc. The sample was dried at 60 °C overnight to remove the guest solvent molecules at 60 °C. Anal. Calcd for $C_{19}H_{10}Y_{0.4}Yb_{0.8}Er_{0.3}O_{12}$: C, 50.49; H, 2.39. Found: C, 50.79; H, 2.43. FT-IR (KBr pellets, $cm^{-1}$): 3061 m, 1693 w, 1570 s, 1488 s, 1411 m, 1286 m, 1257 m, 1138 s, 1042 s, 915 s, 865 s, 776 s, 752 s, 528 s.

**Synthesis of 9 (Y/Yb/Er = 30/40/30)**

A mixture of $Y(NO_3)_3 \cdot 6H_2O$ (0.015 mmol), $Yb(NO_3)_3 \cdot 5H_2O$ (0.02 mmol), $Er(NO_3)_3 \cdot 6H_2O$ (0.015 mmol), $H_4$bptc (0.030 mmol), $H_2$BDC (0.0015 mmol) and 6 mL $H_2O/CH_3OH$ (v/v = 5:1) was added in a 10 mL stainless steel sealed Teflon vial and heated to 150 °C for 72 hours. The reaction vessel was cooled down to room temperature and yellow crystals were collected with ca 56% yield based on $H_4$bptc. The sample was dried at 60 °C overnight to remove the guest solvent molecules at 60 °C. Anal. Calcd for $C_{19}H_{10}Y_{0.5}Yb_{0.5}Er_{0.5}O_{12}$: C, 51.03; H, 2.42.

Found: C, 50.83; H, 2.47. FT-IR (KBr pellets, $cm^{-1}$): 3061 m, 1693 w, 1570 s, 1488 s, 1411 m, 1286 m, 1257 m, 1138 s, 1042 s, 915 s, 865 s, 776 s, 752 s, 528 s.

**X-ray Crystallography**

Single crystal X-ray diffraction measurement was carried out on Bruker SMART APEX-II CCD diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) for **6**. Semi-empirical absorption correction was applied using SADABS program. The structure was solved by direct methods using the SHELXS program of the SHELXTL package and refined with SHELXL.[S1] The final refinement was performed by full matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on $F^2$. Table S3 shows crystallographic data and structure processing parameters. CCDC 1843640 contains the supplementary crystallographic data for the paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

**References**

S1. Sheldrick, G. M. *SHELXL97, Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, **1997**.

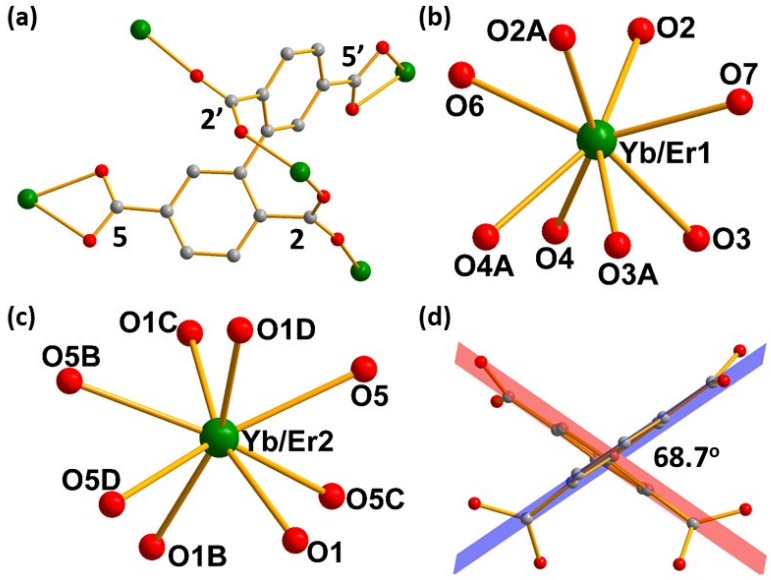


**Fig. S1** (a) The coordination mode of $bptc^{4-}$ ligand. The RE—O bond length (b, c) and dihedral angle (d) between the two benzene rings of $bptc^{4-}$ ligand in compound **6**. Symmetry codes: A = x, y, -z; B = -x, -y, z; C = -x, y, 0.5-z; D = x, -y, 0.5-z.

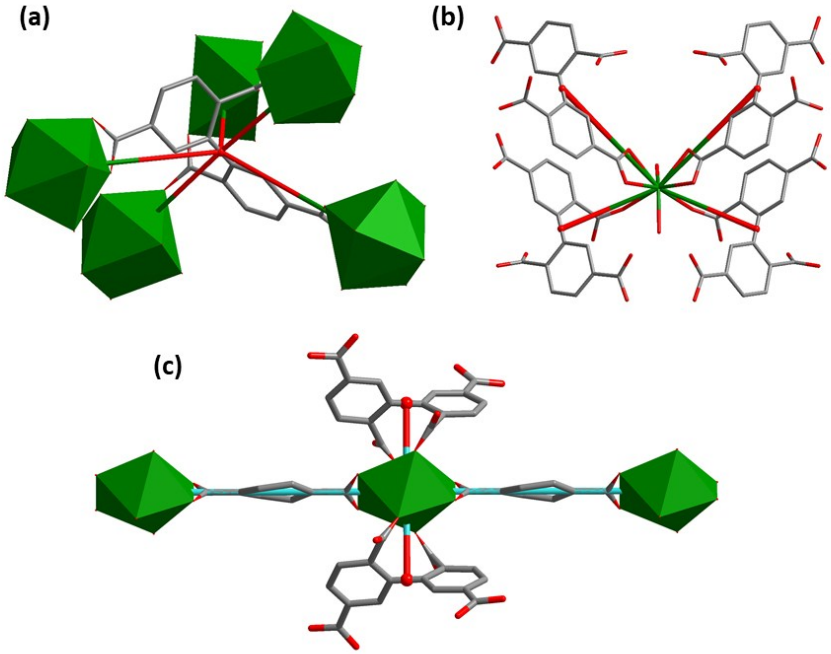


**Fig. S2** Schematic presentations of the 4 (a), 5 (b), and 4 (c) -connected nodes in compound **6**.

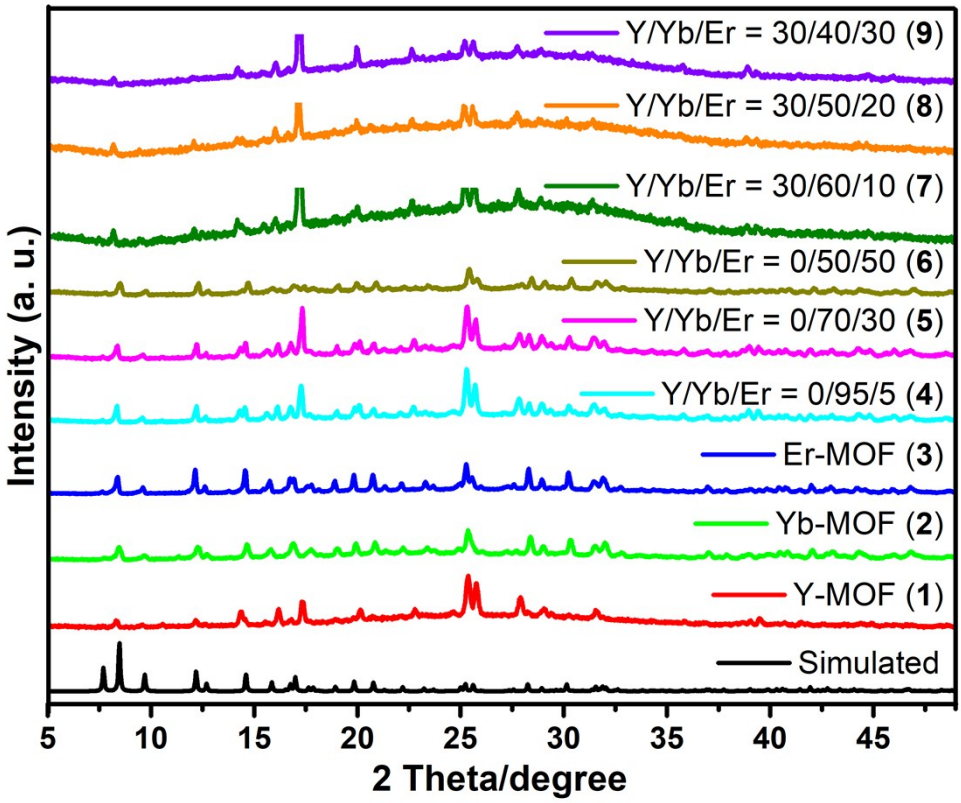


**Fig. S3** The PXRD patterns of the as-synthesized Ln-MOFs and the simulated patterns based on X-ray single-crystal data (black).

**Table S1** Elemental analysis of Y-MOF:Yb/Er.

| Raw ratio | Y (mol%) | Yb (mol%) | Er (mol%) |
|---|---|---|---|
| Y/Yb/Er = 0/95/5 (**4**) | 0 | 91.35 | 8.65 |
| Y/Yb/Er = 0/70/30 (**5**) | 0 | 84.19 | 15.81 |
| Y/Yb/Er = 0/50/50 (**6**) | 0 | 59.32 | 40.68 |
| Y/Yb/Er = 30/40/30 (**7**) | 34.73 | 33.98 | 31.29 |
| Y/Yb/Er = 30/50/20 (**8**) | 28.13 | 52.45 | 19.42 |
| Y/Yb/Er = 30/60/10 (**9**) | 30.12 | 51.78 | 18.10 |

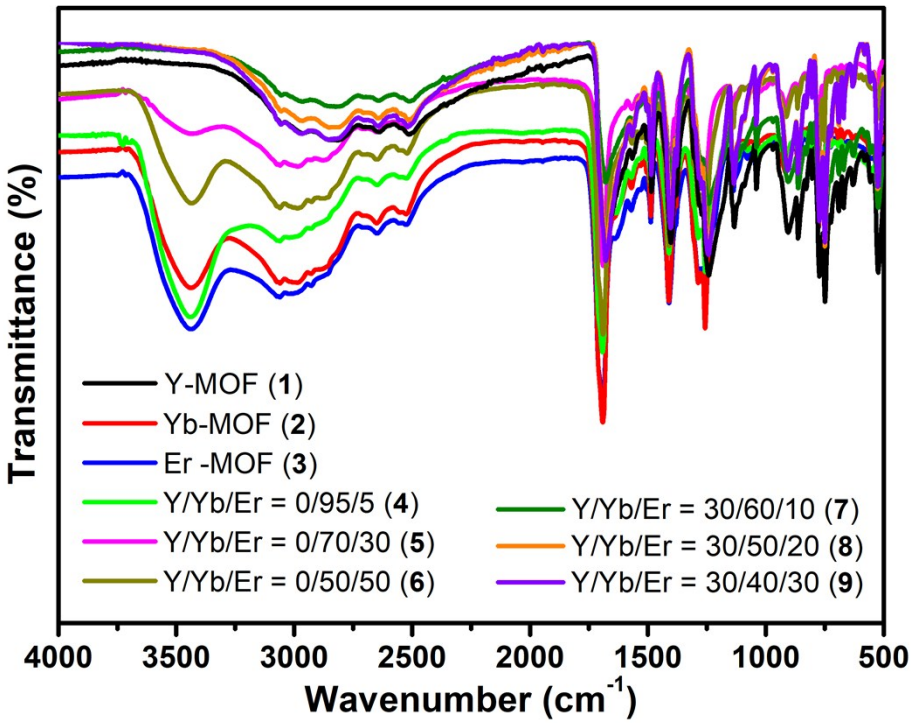


**Fig. S4** IR spectra of compounds **1**-**9**.

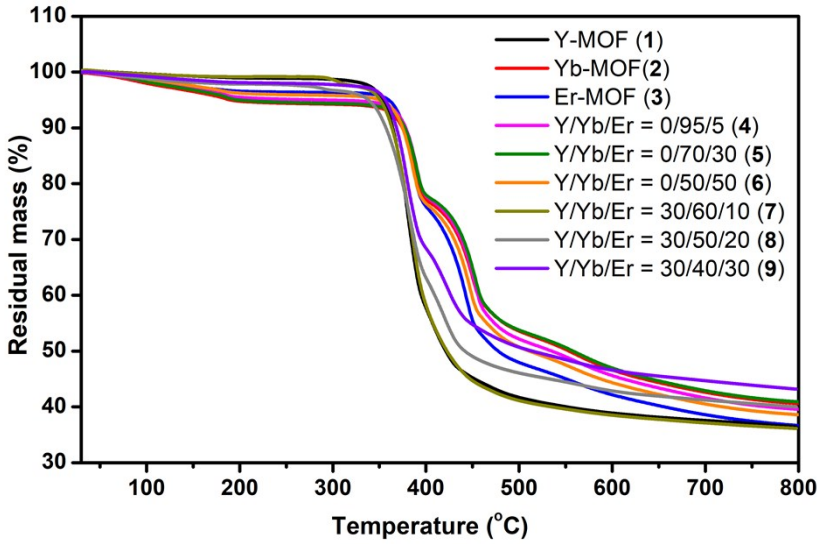


**Fig. S5** Thermogravimetric curves of compounds **1**-**9**.

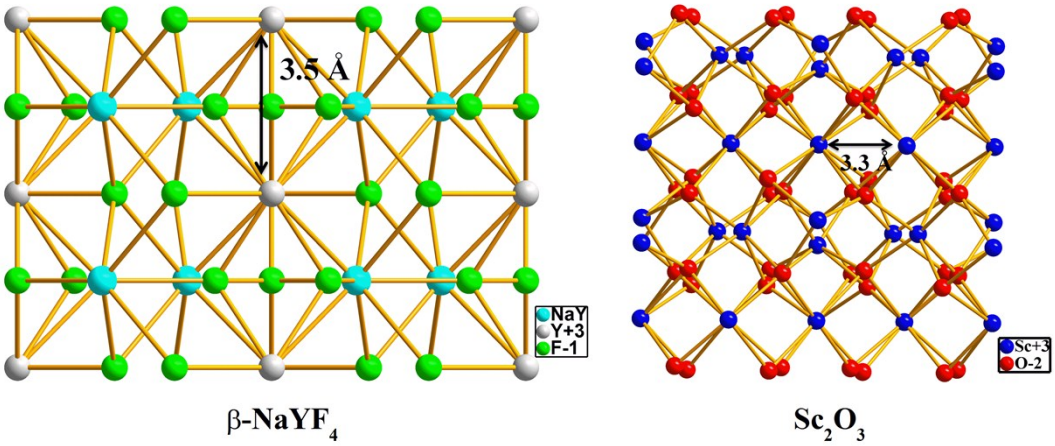


**Fig. S6** The adjacent Ln···Ln distances in the crystal structures of β-$NaYF_4$ and $Sc_2O_3$.

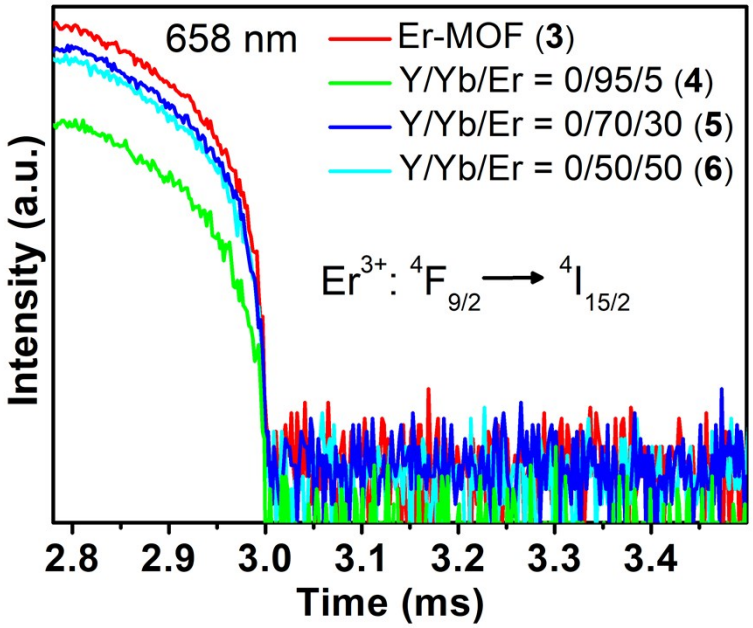


**Fig. S7** Luminescence decay curves of compounds **3-6** at 658 nm emission under 980 nm laser excitation.

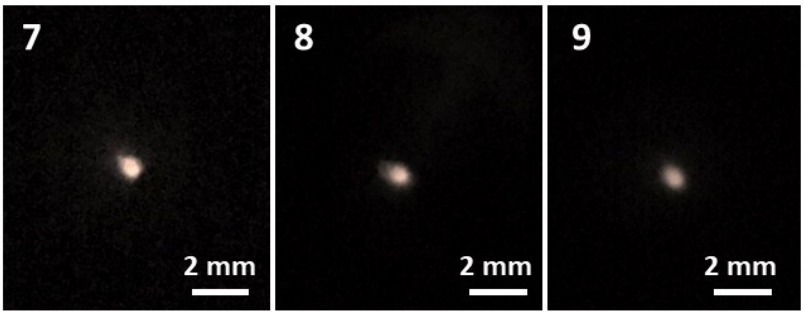


**Fig. S8** The pictures of compounds **7**, **8** and **9** under 980 laser.

**Table S2** Luminescent lifetimes of Y-MOF:Yb/Er at varied doping concentration.

| Er-MOF (**3**) | | |
|---|---|---|
| $\lambda_{em}$ (nm) | 545 | 658 |
| $\tau_1$ (μs) | 358 | 373 |
| $a_1$ (%) | 29.51 | 96.08 |
| $\tau_2$ (μs) | 142 | 15.7 |
| $a_2$ (%) | 70.51 | 3.92 |
| Average Lifetime | 225 | 97 |

| Y/Yb/Er = 0/95/5 (**4**) | | |
|---|---|---|
| $\lambda_{em}$ (nm) | 545 | 658 |
| $\tau_1$ (μs) | 205 | 62.6 |
| $a_1$ (%) | 90.62 | 1.18 |
| $\tau_2$ (μs) | 774 | 118 |
| $a_2$ (%) | 9.37 | 99.82 |
| Average Lifetime | 301 | 104 |

| Y/Yb/Er = 0/70/30 (**5**) | | |
|---|---|---|
| $\lambda_{em}$ (nm) | 545 | 658 |
| $\tau_1$ (μs) | 95.9 | 228 |
| $a_1$ (%) | 42.74 | 49.07 |
| $\tau_2$ (μs) | 275 | 229 |
| $a_2$ (%) | 57.26 | 50.93 |
| Average Lifetime | 271 | 137 |

| Y/Yb/Er = 0/50/50 (**6**) | | |
|---|---|---|
| $\lambda_{em}$ (nm) | 545 | 658 |
| $\tau_1$ (μs) | 560 | 525 |
| $a_1$ (%) | 11.01 | 50.78 |
| $\tau_2$ (μs) | 163 | 111 |
| $a_2$ (%) | 88.91 | 49.20 |
| Average Lifetime | 280 | 112 |

**Table S3** Crystal data and structure refinement details of compound **6**[a].

| | |
|---|---|
| Formula | $C_{19}H_{10}Er_{0.6}Yb_{0.9}O_{12}$ |
| *F*w | 686.35 |
| Crystal system | orthorhombic |
| Space group | *I*bam |
| *a* (Å) | 23.106(3) |
| *b*(Å) | 11.6464(14) |
| *c*(Å) | 18.601(2) |
| *α* (°) | 90 |
| *β* (°) | 90 |
| *γ* (°) | 90 |
| *V* (Å$^3$) | 5008.1(11) |
| *Z* | 8 |
| *μ* (mm$^{-1}$) | 5.405 |
| *Dc* (g/cm$^3$) | 1.855 |
| *R*(int) | 0.0803 |
| GOF on $F^2$ | 0.992 |
| $R_1$[a] [$I > 2\sigma(I)$] | 0.0547 |
| $wR_2$[b] [$I > 2\sigma(I)$] | 0.1316 |

[a] $R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$; [b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma w(F_o^2)^2]^{1/2}$.