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Supporting Information for:

Biocompatible MOFs with High Absolute Quantum Yield for Bioimaging in the Second Near Infrared Window

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Section S1: Experimental details

All chemicals were purchased from commercially available sources and used as received.

Materials

PBS pH 7.2 (Gibco); F-12K Nutrient Mixture (Gibco); heat-inactivated FBS (Equitech-Bio Inc.), Molecular Biology Grade Water (Corning); Dulbecco's Modified Eagle Medium (DMEM, Corning); Cell Titer-Glo 2.0 Assay (Promega), Clear disposable folded capillary cells (Malvern).

Microscope cover glass coverslip, circular #1.5 thickness, FisherSci (Hampton, NH) catalog no. 12-546-2 25CIR-2; Microscope glass slides, 25 x 75 x 1.0 mm, FisherSci (Hampton, NH) catalog no. 12-550-15; 1% poly(vinyl alcohol), Sigma Aldrich (St. Louis, MO) catalog no. 341584; Chemat Technology Spin coater KW-4A.

Powder X-ray Diffraction (PXRD). Measurements were performed on a Siemens Kristalloflex D500 diffractometer, CuKα radiation (λ = 1.54178 Å).

Scanning Electron Microscopy (SEM) - Energy Dispersive Spectroscopy (EDS). SEM analyses were captured on a FEI NovaNano SEM 230, at various accelerating voltages between 1 and 20 kV. EDS analyses were collected on an EDAX Genesis Apex 2 with an Apollo SDD detector.

Transmission Electron Microscopy (TEM). TEM images were taken on JEOL 1200EX transmission electron microscope with a maximum acceleration voltage of 120 kV. Prior

to TEM measurements, samples were dispersed in absolute ethanol and deposited on a carbon film coated copper grid.

Sample activation and gas adsorption measurements. Prior to measuring the gas adsorption isotherms, the samples were immersed in 15 mL of methanol for 3 days, with the solvent replenished every 24 hrs. Following this treatment, all samples were activated under vacuum on a Micromeritics ASAP 2020 surface area and porosity analyzer, at 120° C for 16 hrs. Nitrogen gas adsorption isotherms were measured at 77 K using nitrogen of ultra-high purity (99.999%, obtained from Matheson Tri-Gas).

Sample spin coating. The dried samples were deposited on microscope cover glass by spin coating to create a thin film for microscopic analysis. Approximately 50 micrograms MOF powder was dispersed in 50 μL of a 1% poly(vinyl alcohol) solution (PVOH). A #1.5 thickness circular microscope cover glass was mounted on the spin coater (Chemat Technology Spin Coater, KW-4A) and vacuum was applied. The MOF-PVOH solution was pipetted evenly on the cover glass and then allowed to spin at a low speed of 1000 rpm under vacuum for 60 seconds. The spin coated cover glass was mounted on a microscope slide. Edges of the cover glass were sealed to the microscope slide with clear nail polish.

Photoluminescence (PL) measurements. The NIR PL was collected on spin coated samples dispersed uniformly on a cover glass and placed under the objective. The samples were illuminated with an 808 nm diode laser using a long pass dichroic beam splitter as a

reflector. The PL transmitted through the splitter was directed to an Acton 2500 spectrophotometer (0.5m focal length, 300g/mm grating) equipped with liquid nitrogen cooled InGaAs linear array detector. Both the excitation source and PL were focused through a common 0.65 NA objective.

Quantum yield (QY) measurements. Absolute quantum yield measurements were made by exciting the as-activated samples (activating procedure described in the gas sorption measurement section) with diffuse light at 740 nm in an integrating sphere.[1] Pyrex NMR tubes containing the samples were inserted into the integrating sphere. Both the diffuse 740 nm excitation and the emitted power were simultaneously recorded.

DLS and Zeta Potential Measurements. Hydrodynamic size was acquired on a Malvern Zetasizer Nano-ZS equipped with a He−Ne laser (633 nm) and non-invasive backscatter optics (NIBS). All samples for DLS measurements were suspended in various media (H_2O, 1X PBS, and F-12K media + 10% FBS (by volume)) at 0.1 mg/mL. Measurements were acquired at 25 °C and the refractive index of the material was set to that of silica (1.550). DLS measurements for each sample were obtained in triplicate and the average and standard deviation are reported. The Z-average diameter was used for all reported hydrodynamic size measurements. The zeta potential of each sample was measured in disposable folded capillary cells and measurements were obtained in triplicate with the average and standard deviation reported.

Cell viability assessment. A549 (ATCC) were maintained in F-12K + 10% FBS (by volume) and RAW 264.7 cells (ATCC) were maintained in DMEM + 10% FBS (by volume). For cell viability assessment, 2,500 cells were plated per well in 100μL in 96 well plates and allowed to adhere overnight. After cells had adhered, fresh media containing MOF samples at varied concentration (0-500μg/mL) were prepared. Cell exposure was performed by removing media on the adherent cells and replacing with freshly prepared media containing MOF samples. Cells were exposed to MOF samples for 24 or 48 hours at standard cell culture conditions (37ºC and 5% CO2). After exposure, cell viability was assessed using CellTiter-Glo 2.0 Assay utilizing the standard protocol (Promega) with luminescence measured by a BioTek Synergy neo2 microplate reader. The cell viability was calculated as a percentage of mock treated sample. Cell viability measurements were done in quadruplicate and graphed as the average and standard deviation. Half maximal inhibitory concentration (IC50) was calculated by graphing the cell viability data in Excel and creating an exponential trendline and using the equation of the line to determine the 50% cell viability inhibition dose.

Materials synthesis

Synthesis of compound 1: The reaction mixture containing $Nd(NO_3)_3 \cdot 6H_2O$ (0.0381 g, 0.0869 mmol), $Yb(NO_3)_3 \cdot 5H_2O$ (0.0391 g, 0.0871 mmol), 2,5-dihydroxyterephthalic acid (DOBDC, 0.0544 g, 0.275 mmol), 2-fluorobenzoic acid (2-FBA, 0.249 g, 1.777 mmol), N,N'-dimethylformamide (DMF, 8.8 mL), H_2O (2 mL), HNO_3 (0.2 mL, 3.5 M)

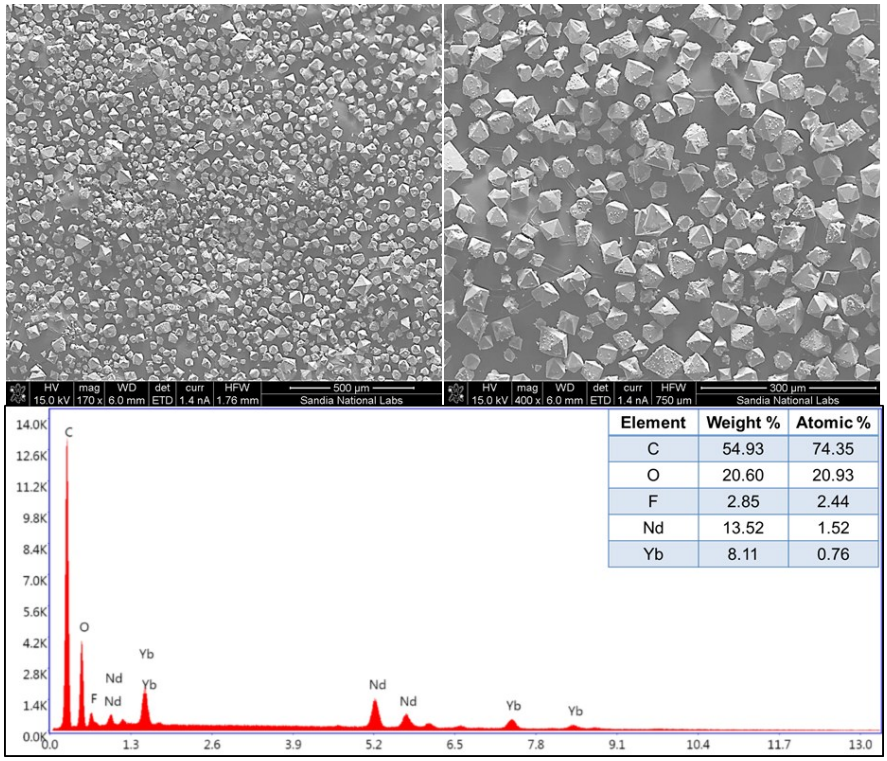
was placed in a 20 mL scintillation vial and was heated to 115 °C for 72 h, at a rate of 1.5°C/minute and cooled to room temperature at a cooling rate of 1°C/minute.

Synthesis of compound 2: The reaction mixture containing $Nd(NO_3)_3 \cdot 6H_2O$ (0.0103 g, 0.0235 mmol), $Yb(NO_3)_3 \cdot 5H_2O$ (0.01055 g, 0.0235 mmol), 2,5-dihydroxyterephthalic acid (DOBDC, 0.0136 g, 0.0686 mmol), 2-fluorobenzoic acid (2-FBA, 0.144 g, 1.0278 mmol), N,N'-dimethylformamide (DMF, 4.0 mL), H_2O (0.5 mL), was placed in a 10 mL microwave vial and was heated to 175 °C for 15 minutes. A CEM Discover SP microwave was used for this experiment.

Synthesis of compound 3: The reaction mixture containing $Nd(NO_3)_3 \cdot 6H_2O$ (0.0103 g, 0.0235 mmol), $Yb(NO_3)_3 \cdot 5H_2O$ (0.01055 g, 0.0235 mmol), 2,5-dihydroxyterephthalic acid (DOBDC, 0.0136 g, 0.0686 mmol), 2-fluorobenzoic acid (2-FBA, 0.240 g, 1.7129 mmol), N,N'-dimethylformamide (DMF, 2.0 mL), H_2O (0.25 mL), was placed in a 10 mL microwave vial and was heated to 175 °C for 3 minutes. Immediately after the temperature of the vial ramped down to 40 °C, a second heating stage was initiated at 175 °C for an additional 1 minute. A CEM Discover SP microwave was used for this experiment.

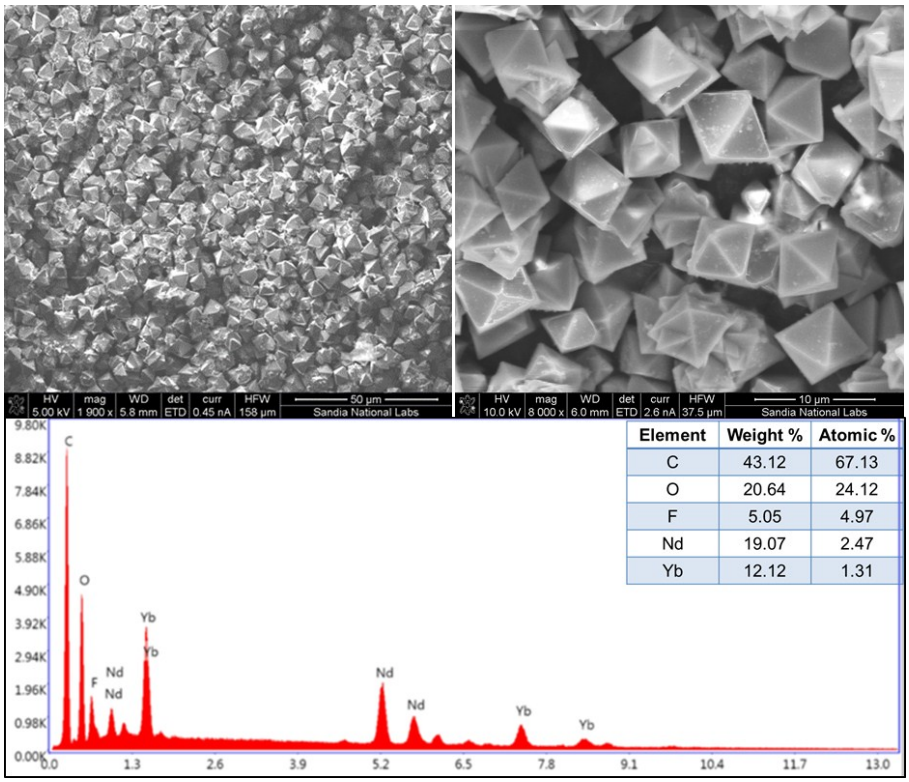
SEM-EDS measurements

Figure S1. SEM-EDS analyses of compound **1**.



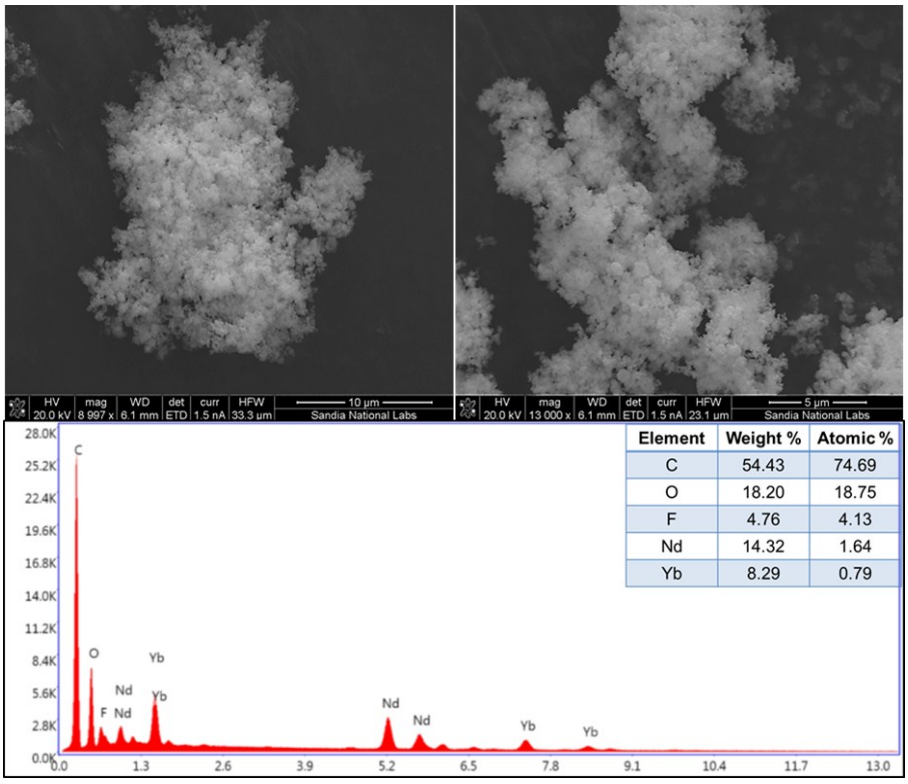
Element	Weight %	Atomic %
C	54.93	74.35
O	20.60	20.93
F	2.85	2.44
Nd	13.52	1.52
Yb	8.11	0.76

Figure S2. SEM-EDS analyses of compound **2**.



Element	Weight %	Atomic %
C	43.12	67.13
O	20.64	24.12
F	5.05	4.97
Nd	19.07	2.47
Yb	12.12	1.31

Figure S3. SEM-EDS analyses of compound **3**.



Element	Weight %	Atomic %
C	54.43	74.69
O	18.20	18.75
F	4.76	4.13
Nd	14.32	1.64
Yb	8.29	0.79

Figure S4. SEM-EDS elemental mapping in compound **3**.

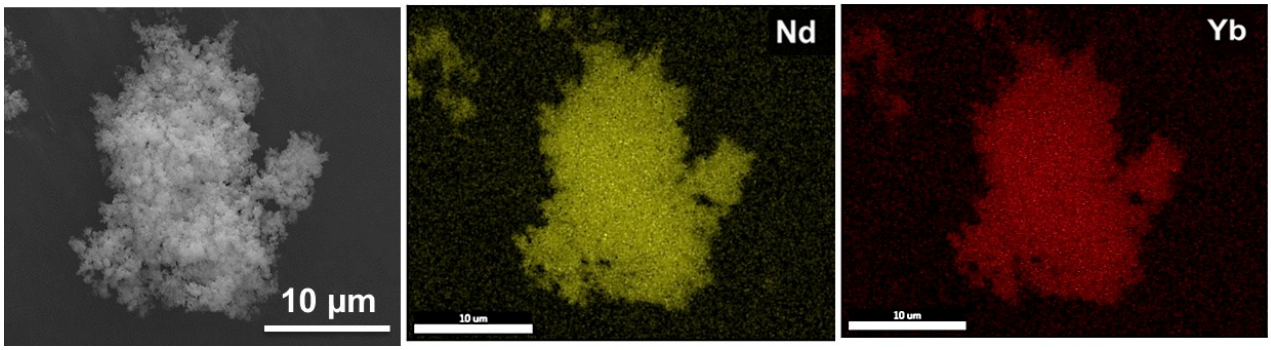
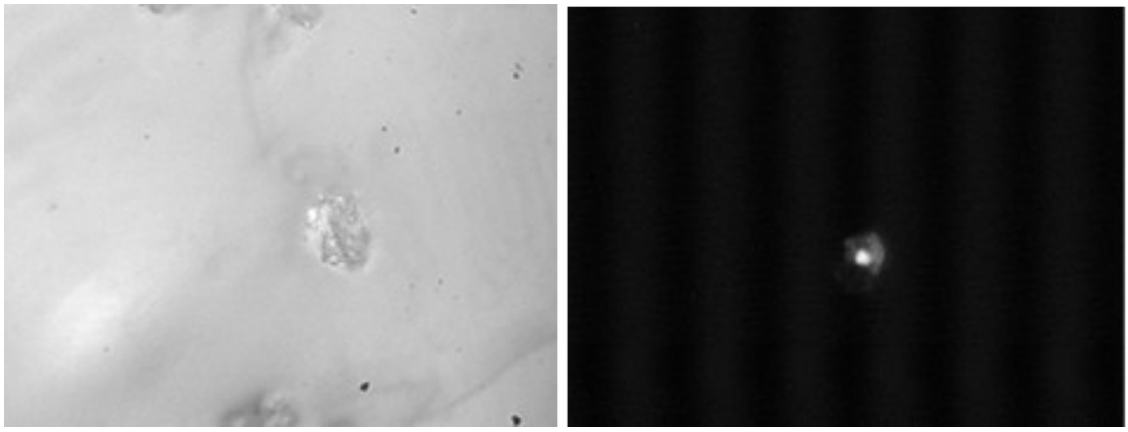


Figure S5. Left: Silicon CCD camera showing an aggregate of crystals illuminated with an 870 nm LED; Right: NIR emission from the sample when excited with an 808 nm laser diode. The emission was detected using a liquid nitrogen cooled InGaAs camera.



References

1. L. S. Rohwer and J. E. Martin, *J. Lumin.*, 2005, **115**, 77-90.