Supporting Information

Ultra-Violet and Electron Beam Irradiation as an Effective Approach for Design of Ln(III) and Am(III) MOFs

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1. Materials and Methods

Caution!

Americium-241 ($T_{1/2}$ = 432.6 years) is a radioactive material that poses a significant health risk if inhaled or ingested. It is an alpha emitter and also releases gamma rays from daughter isotopes (e.g., ^{237m}Np). This radioisotope is dangerous. It must be studied in a facility designed for handling radioactive and toxic heavy metals. Material was manipulated in a negative pressure radiological glovebox, while subsamples were handled within radiological fume hoods.

Chemicals

All chemicals (N,N,-dimethylformamide (DMF), nitric acid, lanthanum nitrate hexahydrate, neodymium nitrate hexahydrate, praseodymium nitrate hexahydrate, europium nitrate hexahydrate, gadolinium nitrate hexahydrate, terbium nitrate hexahydrate, thulium nitrate hexahydrate, ytterbium nitrate hexahydrate, trifluoroacetic anhydride (TFA) was purchased from Rushim and 4,4′,4″,-Benzene-1,3,5-triyl-tris(benzoic acid) (H_3BTB) was purchased from Macklin. $^{241}AmO_2$ (isotope pure grade) was purchased from Isotope JSC. The reagents were used without further purification.

General procedure

Am stock solution: 10 mg of AmO_2 was dissolved in 3 mL of 15 M HNO_3 with addition of 20 μL of 30 wt.% H_2O_2 solution. The obtained orange-pink solution was evaporated leading to the formation of pink wet salts. Observed crystals was fully dissolved in 1 mL of 8 M HNO_3 and resulting orange solution was diluted by distilled water to a concentration of [Am^{3+}] equal to 0.021 M.

Solvothermal procedure

Am-MIL-103: 164 μL of Am stock solution was evaporated forming pink crystals that was mixed up with 1.5 mg of H_3BTB and then fully dissolved in 100 μL DMF. After that, 5 μL 14 M HNO_3, 8 μL TFA and 100 μL DMF were added. The deep orange solution was torch-sealed in a glass ampoule and heated in oven to 160 °C for 24 hours. Suitable for SCXRD orange-pink prismatic crystals, exhibiting the alexandrite effect, were observed and removed from the mother liquor via decantation and washed by fresh DMF 3 times. Calc. y. 24%. Photographs of the crystals are shown in Figure S7

Photochemical synthesis of 2D-Ln-BTB

The solutions were irradiated using "Alfa-11" pulsed ultraviolet equipment (NPP Melitta). The pulse frequency in all experiments was 3 Hz.

The photon flux was determined using a ferrioxalate actinometer (https://hepatochem.com/standard-ferrioxalate-actinometer-protocol/). A 3 ml actinometric solution was exposed in the range of 2–28 seconds to a Xe pulsed UV lamp within 10-mm quartz cuvette. The optical density of irradiated solutions was measured using a Varian Cary 100 UV-Vis spectrophotometer at a wavelength of 510 nm (Figure S8). The total light flux intensity in the wavelength range of 200–450 nm is $I = 2.4\times10^{22}$ quanta m^{-2} s^{-1}).

Ln stock solution: 30 mg H_3BTB and 30 mg $Ln(NO_3)_3\times6H_2O$ were dissolved in the mixture of 2.7 ml DMF and 0.3 ml H_2O.

2D-Ln-MOFs. A 3 ml aliquote of Ln stock solution was exposed to a Xe pulsed UV lamp within 10-mm quartz cuvette. The temperature of the solution was maintained at no higher than 30°C, and the initial pH of the solutions was approximately 4.0–4.5. The formation of precipitates was observed after 20 minutes of irradiation. The precipitate was separated from the solution through a centrifugation and was subsequently washed thrice with pure DMF, methanol, and ether, respectively. The resulting material was then dried at 60 °C. FTIR bands for UV-2D-Ln-BTB, cm^{-1}: La – 548(w), 608(w), 669(w), 708(w), 782(m), 810(w), 857(m), 1015(w), 1061(w), 1092(shoulder, w), 1107(w), 1142(w), 1180(w), 1250(w), 1307(w), 1401(asym, vs), 1512(shoulder, w), 1532(s), 1586(s), 1605(s), 1655(asym, s), 1717(w), 2928(w), 3056(w); Tb – 556(w), 610(w), 671(w), 706(w)783(m), 814(w), 860(m), 1015(w), 1061(w), 1092(shoulder, w), 1107(w), 1146(w), 1181(w), 1250(w), 1312(w), 1385(shoulder, s), 1412(vs), 1512(shoulder, s), 1532(s), 1586(s), 1605(s), 1659(asym, s), 1713(w), 2928(w), 3063(w), 3179(br, w), 3604(w). FTIR spectra are shown in the Figure S4b. The CHN-analysis was performed for La and Eu MOFs (see Table S1).

Table S1. Calculated and experimental CHN content for UV-2D-Ln-BTB

Element	La		Eu	
	Calc., %	Exp., %	Calc., %	Exp., %
C	54.7	49.8	53.6	47.3
H	2.9	3.3	2.8	3.7
N	0	0.02	0	0.7

UV-Am-MIL-103: 330 µL of Am stock solution was mixed up with 3 mg of H_3BTB and then fully dissolved in 1 mL DMF. The exposure was carried out in accordance with protocols

developed for lanthanides. The product yield is approximately 30% (due to the small scale of the product yields may contain significant error).

Radiation-induced synthesis

Irradiation experiments have been carried out on a linear electron accelerator LINS 3-350. The energy of electron beam flow was 3 MeV. Dose rate varied from 8.4 to 180 Gy/s. The pulse frequency was varied from 10 to 50 Hz. The dose rate was determined using a Frike liquid dosimeter. To exclude the influence of the geometric parameters of the holder, dosimetry was performed in holders similar to those used in the main experiment with the same volume of solution. The absorbed dose was recalculated taking into account the solvent (90% DMF, 10% water).

Rad-Ln-MIL-103: A 3-ml stock solution of Ln was placed into a 10-mm glass tube. The solution was deaerated and sealed. FTIR bands for rad-La-MIL-103, cm^{-1}: 20 Gy/s – 544(w), 606(w), 667(w), 706(w), 783(m), 810(w), 857(m), 1015(w), 1061(w), 1103(asym, w), 1146(w)1181(w), 1254(w), 1281(w), 1304(w), 1397(asym, vs), 1509(shoulder, s), 1532(s), 1582(s), 1605(s), 1655(s), 1717(w), 2928(w), 3060(w), 3430(asym, br, m); 180 Gy/s – 544(w), 667(w), 706(w), 779(m), 814(w), 857(asym, m), 1014(w), 1107(w), 1146(w), 1184(w), 1246(w), 1280(w), 1308(w), 1404(asym, vs), 1524(asym, s), 1582(s), 1605(s), 1655(w), 1721(w), 2925(w), 3063(w), 3376(br, w), 3607(w). FTIR spectra are shown in the Figure S4a. The CHN-analysis was performed for La and Eu MOFs (see Table S2).

Table S2. Calculated and experimental CHN content for rad-Ln-MIL-103

Element	La		Gd	
	Calc., %	Exp., %	Calc., %	Exp., %
C	54.7	50.4	53.1	51.5
H	2.9	4.2	2.8	3.9
N	0	4.0	0	1.0

Rad-Am-MIL-103: 3 mg of H_3BTB was fully dissolved in mixture obtained by mixing 330 μL of Am stock solution and 1.5 mL DMF and torch-sealed in glass ampoule under vacuum.

Characterization

SCXRD

The single crystal X-ray diffraction experiment was performed on a Bruker KAPPA APEX II diffractometer. The cell parameters were refined over the entire data set together with data reduction by using SAINT-Plus software [1]. Absorption corrections were introduced using the

SADABS program [2]. The structure was solved using the SHELXT-2018/2 program [3] and refined by full-matrix least squares on F^2 in the anisotropic approximation only for Am atom in the SHELXL-2018/3 program [4]. The C and O atoms were refined isotropically due to poor data quality. The H atoms were located in geometrically calculated positions and refined with isotropic temperature factors equal to 1.2 U_{eq}(C) and 1.5 U_{eq}(O). Solvent molecules were strongly disordered and so their contribution to the reflection intensity was removed using the SQUEEZE routine of PLATON [5], and the structure was then refined again using the data generated. Crystal data, data collection, and structure refinement details are summarized in Table S3. The structure was deposited at the Cambridge Crystallographic Data Centre (CCDC № 2503007).

pXRD

The XRD study was performed on a Panalytical X'Pert Pro MPD diffractometer (Netherlands), equipped with a Cu-Kα X-ray source (λ = 1.54184 Å) and an X'celerator detector, operating under the following conditions: voltage: 40 kV; current: 40 mA; range: 2°–60°; step size: 0.022°.

Thermal analysis

Thermal gravimetry (TG) with simultaneous differential thermal analysis (DTA) was performed using a Netzsch STA Jupiter 449 F3 thermoanalytical complex equipped with QMS 403 Aëolos Quadro Coupling mass-spectrometer. The heating rate was set at 10 °C/min, spanning the temperature range from 40 °C to 1000 °C. The experiment utilized Al2O3 crucibles, with the atmosphere composed of a synthetic air.

FTIR spectroscopy

Infrared spectra of the compounds were recorded using the FT-801 IR Fourier spectrometer-microscope (Simex, Russia) equipped with Mercury Cadmium Telluride (MCT) detector in transmission mode from KBr pellets in the range of 4000-500 cm^{-1} with a resolution of 4 cm^{-1}.

Scanning electron microscopy and EDX spectroscopy

Micrographs of the samples were obtained using a Kyky-EM6900 scanning electron microscope at an accelerating voltage of 20 kV in SE and BSE modes. The elemental composition and distribution maps were obtained using an Oxford INCA Energy Dispersive X-ray Spectrometer (EDX).

2. SCXRD

Table S3. Crystal data and structure refinement for **Am-MIL-103.**

Identification code	Am-MIL-103
CCDC number	2503007
Empirical formula	$C_{27}H_{17}AmO_7$
Formula weight	696.41
Temperature/K	100(2)
Crystal system	trigonal
Space group	R32
a/Å	28.767(2)
b/Å	28.767(2)
c/Å	12.2277(16)
α/°	90
β/°	90
γ/°	120
Volume/Å^3	8763.4(17)
Z	9
ρ_{calc}g/cm^3	1.188
μ/mm^{-1}	1.997
F(000)	2970.0
Crystal size/mm^3	0.36 × 0.08 × 0.06
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	8.502 to 49.994
Index ranges	$-34 \leq h \leq 34$, $-34 \leq k \leq 34$, $-14 \leq l \leq 14$
Reflections collected	26642
Independent reflections	3429 [R_{int} = 0.1458, R_{sigma} = 0.0973]
Data/restraints/parameters	3429/0/76
Goodness-of-fit on F^2	1.016
Final R indexes [I>=2σ (I)]	R_1 = 0.0545, wR_2 = 0.1140
Final R indexes [all data]	R_1 = 0.0631, wR_2 = 0.1176
Largest diff. peak/hole / e Å^{-3}	2.39/-1.86
Flack parameter	-0.09(2)

Table S4. Bond Lengths for **Am-MIL-103.**

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Am1	O4	2.528(7)		C9	C10	1.423(17)
Am1	O4[1]	2.528(7)		C11	C12	1.390(17)
Am1	O3[2]	2.467(7)		C11	C10	1.423(17)
Am1	O3[1]	2.706(7)		C4	C5	1.418(14)
Am1	O3[3]	2.467(7)		C12	C7	1.383(17)
Am1	O3	2.706(7)		C8	C7	1.388(17)
Am1	O1	2.424(9)		C6	C7	1.509(16)
Am1	O1[1]	2.424(9)		C16	C13[4]	1.373(15)
Am1	O2	2.469(15)		C16	C13	1.373(15)
O4	C6	1.261(13)		C2	C1	1.49(2)
O3	C6	1.278(14)		C5	C15[5]	1.51(2)
O1	C1	1.248(12)		C10	C13	1.487(17)
C3	C4	1.380(17)		C14	C13	1.402(18)
C3	C2	1.408(14)		C14	C15	1.376(15)
C9	C8	1.333(17)				

[1]4/3-X,2/3-X+Y,2/3-Z; [2]2/3-Y+X,4/3-Y,1/3-Z; [3]2/3+Y-X,4/3-X,1/3+Z; [4]-1/3+Y,1/3+X,1/3-Z; [5]-1/3+X,-2/3+Y,1/3+Z

Table S5. Bond Angles for Am-MIL-103.

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
O4[1]	Am1	O4	75.7(4)		Am1[4]	O3	Am1	104.9(3)
O4[1]	Am1	O3	66.9(2)		C6	O3	Am1	87.8(6)
O4[1]	Am1	O3[1]	49.8(2)		C6	O3	Am1[4]	130.3(7)
O4	Am1	O3	49.8(2)		C1	O1	Am1	129.5(8)
O4	Am1	O3[1]	66.9(2)		C4	C3	C2	122.7(12)
O3[2]	Am1	O4	76.6(2)		C8	C9	C10	121.7(12)
O3[3]	Am1	O4	135.4(2)		C12	C11	C10	119.1(11)
O3[2]	Am1	O4[1]	135.4(2)		C3	C4	C5	118.9(11)
O3[3]	Am1	O4[1]	76.6(2)		C7	C12	C11	121.2(11)
O3[1]	Am1	O3	97.9(3)		C9	C8	C7	121.1(12)
O3[2]	Am1	O3[1]	139.97(12)		O4	C6	O3	121.2(10)
O3[3]	Am1	O3[1]	68.5(3)		O4	C6	C7	118.8(10)
O3[2]	Am1	O3	68.5(3)		O3	C6	C7	119.7(10)
O3[3]	Am1	O3	139.97(12)		C13	C16	C13[5]	120.4(16)
O3[3]	Am1	O3[2]	144.7(3)		C12	C7	C8	119.3(11)
O3[2]	Am1	O2	72.33(17)		C12	C7	C6	119.2(11)
O3[3]	Am1	O2	72.33(17)		C8	C7	C6	121.4(11)
O1	Am1	O4[1]	121.8(3)		C3	C2	C3[6]	116.8(15)
O1	Am1	O4	76.2(3)		C3[6]	C2	C1	121.6(8)
O1[1]	Am1	O4	121.8(3)		C3	C2	C1	121.6(8)
O1[1]	Am1	O4[1]	76.2(3)		C4	C5	C4[6]	120.0(15)
O1	Am1	O3[1]	72.3(3)		C4[6]	C5	C15[7]	120.0(8)
O1[1]	Am1	O3	72.3(3)		C4	C5	C15[7]	120.0(8)
O1[1]	Am1	O3[1]	122.8(3)		C9	C10	C13	123.1(11)
O1	Am1	O3[3]	89.9(3)		C11	C10	C9	117.4(11)
O1	Am1	O3	122.8(3)		C11	C10	C13	119.5(11)
O1[1]	Am1	O3[2]	89.9(3)		C15	C14	C13	121.6(12)
O1	Am1	O3[2]	83.8(3)		C16	C13	C10	119.0(12)

O1[1]	Am1	O3[3]	83.8(3)		C16	C13	C14	119.3(12)
O1	Am1	O1[1]	159.0(4)		C14	C13	C10	121.7(11)
O1	Am1	O2	79.5(2)		O1	C1	O1[6]	125.1(17)
O1[1]	Am1	O2	79.5(2)		O1[6]	C1	C2	117.4(8)
O2	Am1	O4	142.15(18)		O1	C1	C2	117.4(8)
O2	Am1	O4[1]	142.14(18)		C14	C15	C5[8]	121.1(8)
O2	Am1	O3[1]	131.04(16)		C14[5]	C15	C5[8]	121.1(8)
O2	Am1	O3	131.04(16)		C14	C15	C14[5]	117.9(16)
C6	O4	Am1	96.4(6)					

[1]4/3-X,2/3-X+Y,2/3-Z; [2]2/3-Y+X,4/3-Y,1/3-Z; [3]2/3+Y-X,4/3-X,1/3+Z; [4]4/3-Y,2/3+X-Y,-1/3+Z; [5]-1/3+Y,1/3+X,1/3-Z; [6]+Y,+X,1-Z; [7]-1/3+X,-2/3+Y,1/3+Z; [8]1/3+X,2/3+Y,-1/3+Z

Table S6. Torsion Angles for **Am-MIL-103.**

A	B	C	D	Angle/°		A	B	C	D	Angle/°
Am1	O4	C6	O3	23.4(11)		C9	C10	C13	C14	-36.5(17)
Am1	O4	C6	C7	-150.0(9)		C11	C12	C7	C8	0.7(18)
Am1[1]	O3	C6	O4	86.2(12)		C11	C12	C7	C6	176.9(10)
Am1	O3	C6	O4	-21.6(10)		C11	C10	C13	C16	-37.4(15)
Am1[1]	O3	C6	C7	-100.5(11)		C11	C10	C13	C14	143.1(12)
Am1	O3	C6	C7	151.7(9)		C4	C3	C2	C3[2]	0.4(8)
Am1	O1	C1	O1[2]	34.2(6)		C4	C3	C2	C1	-179.6(8)
Am1	O1	C1	C2	-145.8(6)		C12	C11	C10	C9	-0.2(17)
O4	C6	C7	C12	-3.6(16)		C12	C11	C10	C13	-179.8(11)
O4	C6	C7	C8	172.5(11)		C8	C9	C10	C11	3.0(17)
O3	C6	C7	C12	-177.1(10)		C8	C9	C10	C13	-177.3(11)
O3	C6	C7	C8	-0.9(17)		C2	C3	C4	C5	-0.8(16)
C3	C4	C5	C4[2]	0.4(8)		C10	C9	C8	C7	-4.1(19)
C3	C4	C5	C15[3]	-179.6(8)		C10	C11	C12	C7	-1.6(18)
C3[2]	C2	C1	O1[2]	-28.0(7)		C13[4]	C16	C13	C10	-179.7(12)
C3	C2	C1	O1[2]	152.0(7)		C13[4]	C16	C13	C14	-0.2(8)
C3	C2	C1	O1	-28.0(7)		C13	C14	C15	C5[5]	179.8(8)
C3[2]	C2	C1	O1	152.0(7)		C13	C14	C15	C14[4]	-0.2(8)
C9	C8	C7	C12	2.2(18)		C15	C14	C13	C16	0.5(16)
C9	C8	C7	C6	-174.0(11)		C15	C14	C13	C10	180.0(9)
C9	C10	C13	C16	143.0(11)						

[1]4/3-Y,2/3+X-Y,-1/3+Z; [2]+Y,+X,1-Z; [3]-1/3+X,-2/3+Y,1/3+Z; [4]-1/3+Y,1/3+X,1/3-Z; [5]1/3+X,2/3+Y,-1/3+Z

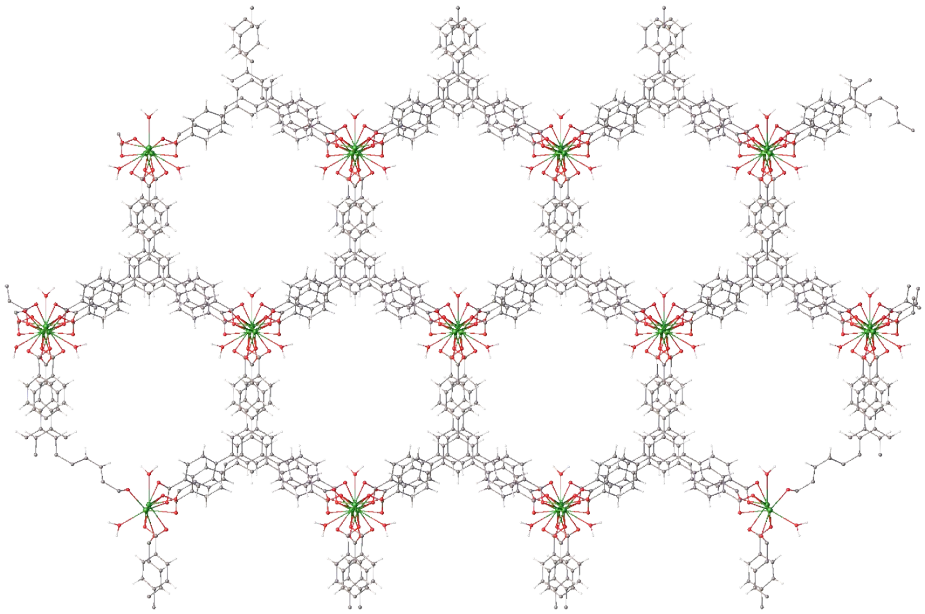

Figure S1. Crystal packing of structure **Am-MIL-103**.

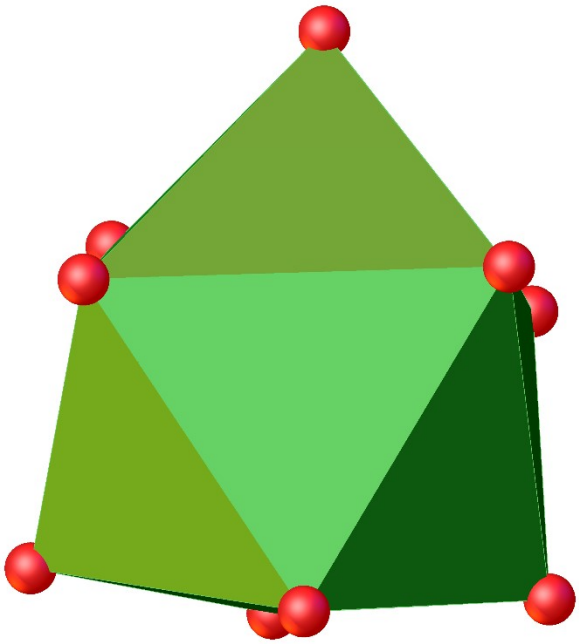

Figure S2. Coordination of the Am atom in structure **Am-MIL-103**.

3. pXRD

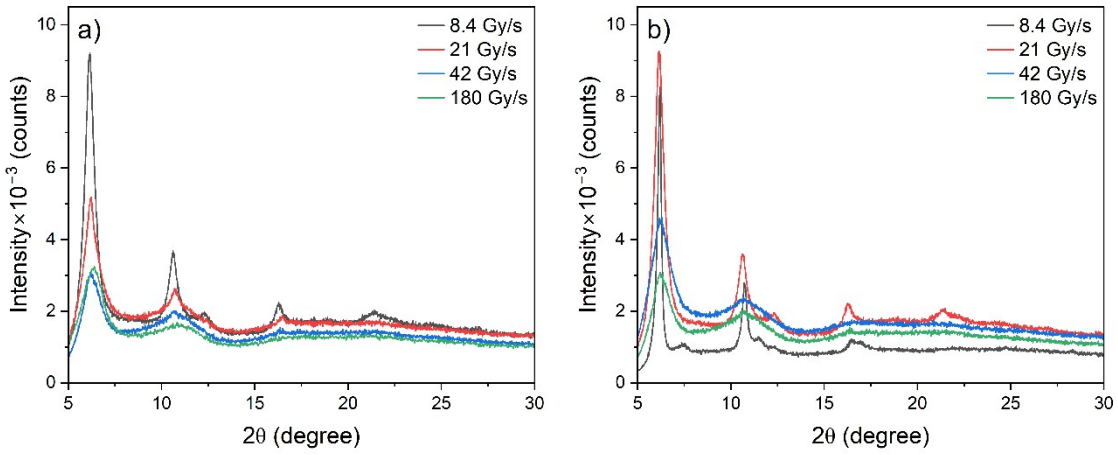

Figure S3. XRD patterns of rad-La-MIL-103 synthesized under vacuum (a) and in air (b) with various dose rate. Irradiation dose in all samples was 200 kG except for 8.4 dose rate.

4. FTIR spectroscopy

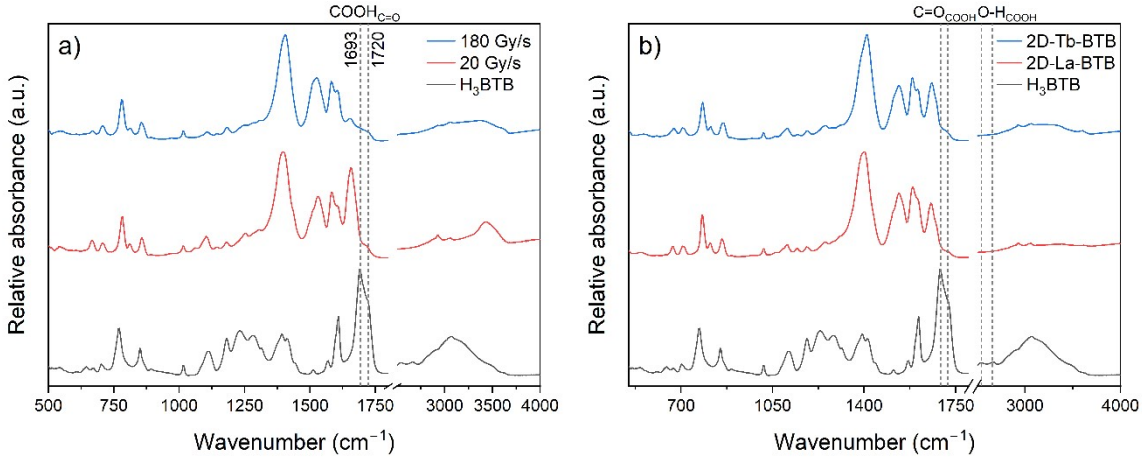

Figure S4. FTIR spectra: a) rad-La-MIL-103; b) UV-2D-La-BTB and UV-2D-Tb-BTB.

5. SEM and EDX analysis

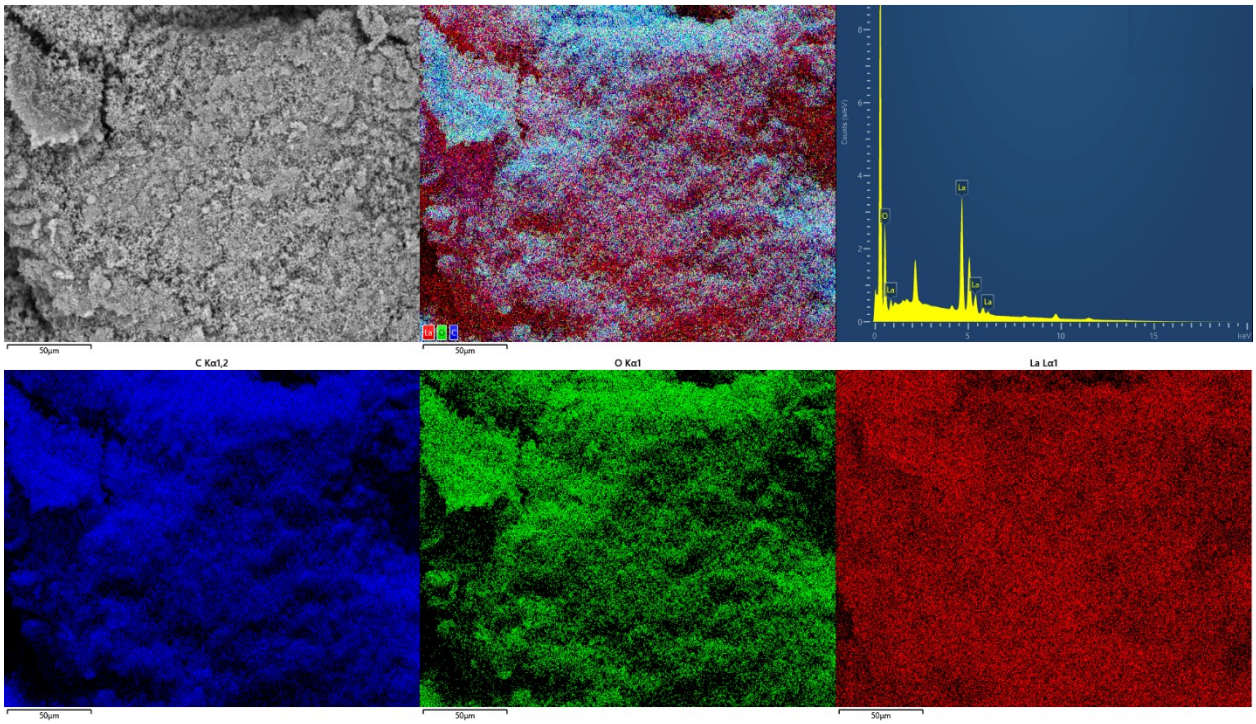

Figure S5. BSE SEM image, multilayer elements map, EDX spectrum and C, O and La distribution of rad-La-MIL-103 MOF.

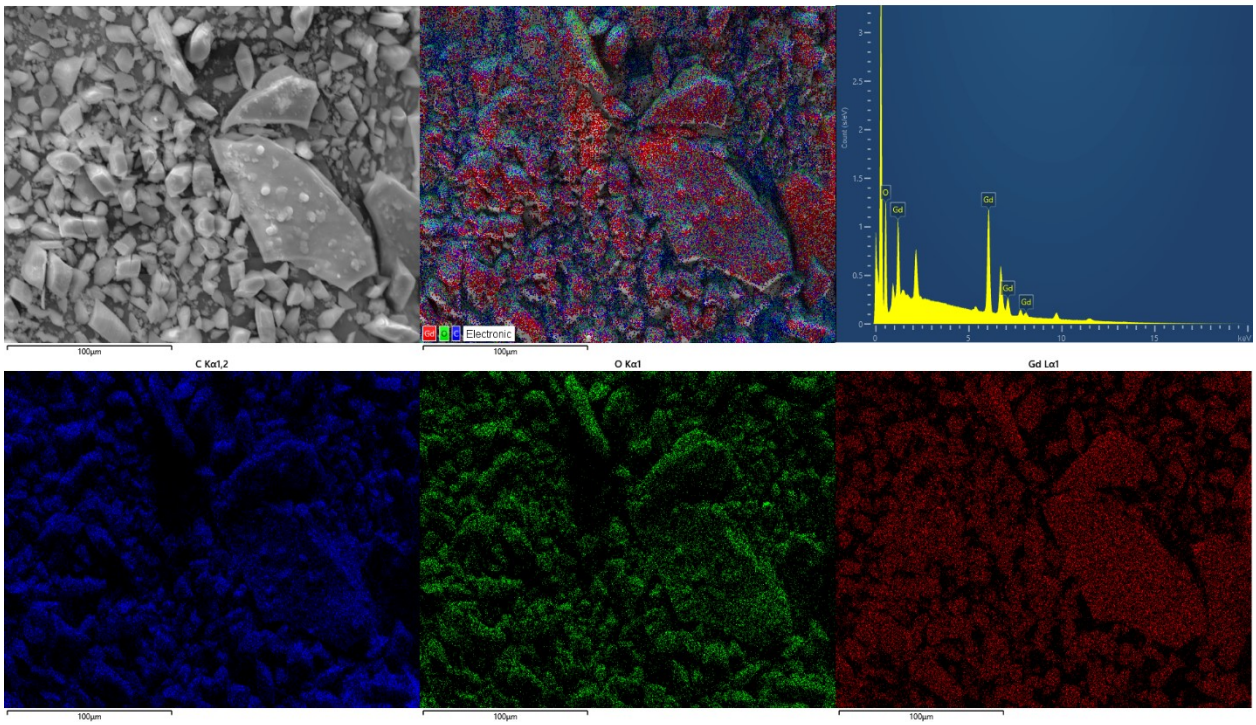

Figure S6. BSE SEM image, multilayer elements map, EDX spectrum and C, O and La distribution of UV-2D-Gd-BTB MOF.

Table S7. Elemental composition of rad-La-MIL-103 and UV-2D-Gd-BTB MOFs by EDX spectroscopy.

Element	Rad-La-MIL-103			UV-2D-Gd-BTB		
	At., %.	**Wt., %**	**σ**	**At., %.**	**Wt., %**	**σ**
C	80.49	65.43	0.08	79.59	62.47	0.12
O	17.89	19.37	0.08	18.66	19.51	0.11
Ln	1.62	15.20	0.04	1.75	18.02	0.08

6. Crystal images of Am-MIL-103

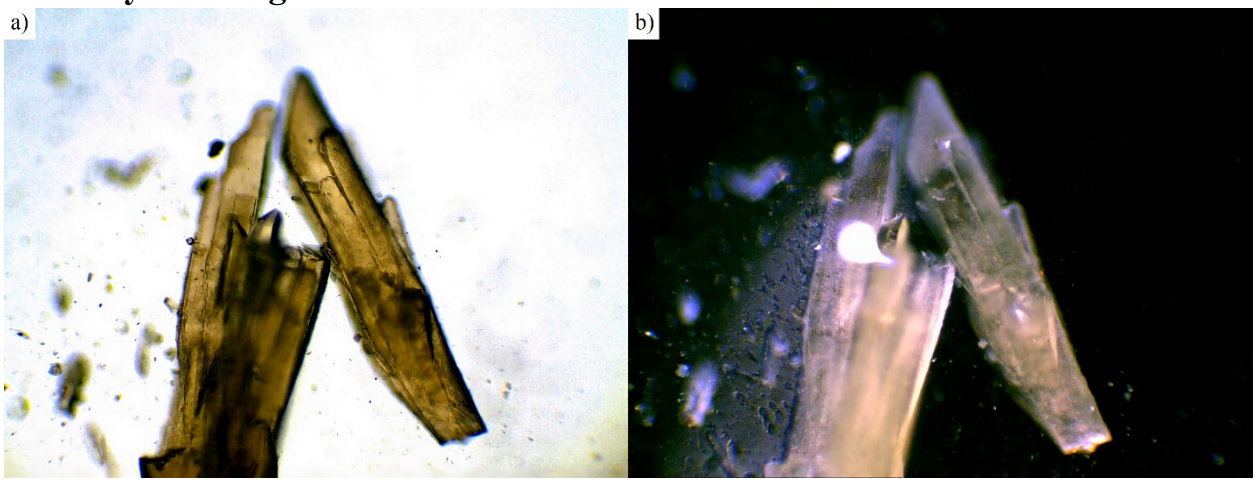

Figure S7. Images of the **Am-MIL-103** crystal: a) in transmission and b) reflected light.

7. STY of MOFs

Table S8. The space-time yield of MOFs.

Sample	Condition	The space-time yield ($kg \cdot m^3 \cdot d^{-1}$)*	Reference
UV-2D-Ln-MOF	UV (2 h, RT)	6300	This work
UV-La-MIL-103	UV (2 h, T = 70 °C)	6300	This work
rad-La-MIL-103	EB (300 kGy, 180 Gy/s, 3 MeV, RT)	17000	This work
rad-La-MIL-103	EB (90 kGy, 8.4 Gy/s, 3 MeV, RT)	8800	This work
La-MIL-103	Solvothermal (24 h, 160 °C)	390	This work
ZIF-8	EB (50 kGy, 625 Gy/s, 1.5 MeV RT)	45000	10.1002/anie.202212532
Zeolites	-	50-150	Chem. Soc. Rev., 2009, 38, 1284–1293

* STY calculated using mass of as-synthesized product.

8. Actinometry

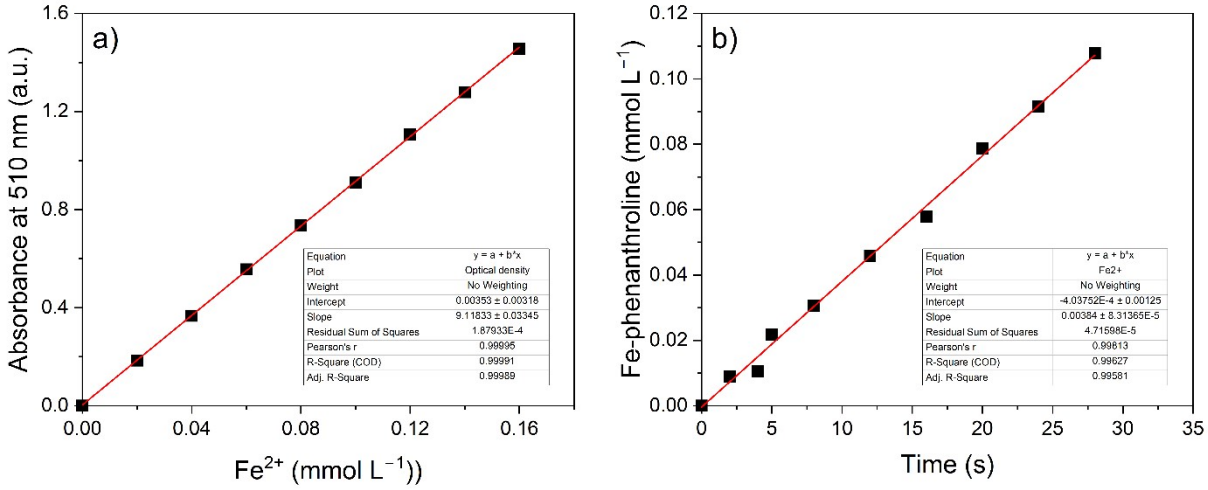

Figure S8. Determination of Fe-phenanthroline complex concentration in irradiated solution: a) Calibration curve, b) Concentration of Fe-phenanthroline comlex after various time of irradiation actinometric solution.