Supporting Information for:

Intrinsic Broadband White-Light Emission by a Tuned, Corrugated Metal-Organic Framework

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Section S1: Materials and methods

All materials were purchased from commercially available sources, and used without further purification.

Synthesis of SMOF-1

The reaction mixture containing $In(NO_3)_3 \cdot 5H_2O$ (0.0435mmol, 0.017g), 1,3,5-Tris(4-carboxyphenyl)benzene (BTB) (0.0435mmol, 0.019g) and oxalic acid (OA) (0.065mmol, 0.00585g), DEF (2mL), EtOH (3.25 mL) was placed in a 20 mL scintillation vial and was heated to 115°C for 4 days, at a rate of 1.5°C/minute and cooled to room temperature at a cooling rate of 1°C/minute.

Synthesis of 10% Eu-SMOF-1

The reaction mixture containing $In(NO_3)_3 \cdot H_2O$ (0.0435mmol, 0.0017g), $EuCl_3 \cdot 6H_2O$ (0.00435 mmol, 0.0016 g), 1,3,5-Tris(4-carboxyphenyl)benzene (BTB) (0.0435mmol, 0.0019g) and oxalic acid (OA) (0.065mmol, 0.00585g), DEF (2mL), EtOH (3.25 mL) was placed in a 20 mL scintillation vial and was heated to 115°C for 4 days, at a rate of 1.5°C/minute and cooled to room temperature at a cooling rate of 1°C/minute.

Section S2: X-ray single-crystal data collection and determination

The X-ray intensities were measured using a Bruker-APEX/CCD diffractometer (Mo Kα ,λ = 0.71073 Å). Indexing and frame integration was performed using the APEX-II software suite.[S1] Absorption correction was performed using face-indexing (numerical method) also within the APEX-II software. The structure was solved and refined using SHELXS-97 contained in SHELXTL v6.10 packages.[S2] The hydrogen atoms were placed in geometrically calculated positions and included in the refinement process using a riding model.

The BTB ligand illustrated some difficulty in the refinement of carbon atoms. Since the BTB molecule is fairly well defined as it contains 4 benzene rings, the carbon atoms within this ligand were restrained to exhibit the proper bond lengths (and angles) for this compound. In addition, each benzene ring in the BTB ligand was assumed to be planar, and therefore individual rings within the BTB molecule were restrained to be flat. Also, the bond distances between the O and C atoms at the termination of the BTB ligand were restrained. These restraints added considerable stability to the refinement.

There was significant scatter from the voids which suggested the presence of solvent guest molecules. Solvent density was detected at two different crystallographic locations in fractional coordinates: Site 1 at (0.214, -0.024, -0.015) and Site 2 at (0.715, 0.871, 0.920). Attempts to refine the highly disordered solvent were unproductive. Therefore, the program Platon/Squeeze[S3] was employed to model the solvent presence. Thermogravimetric analysis (TGA) coupled with Mass-Spectrometry (MS) revealed mass

loss equivalent to diethylformamide (DEF), which was employed in the crystallization process. The application of the Squeeze routine reported solvent accessible void space of 20985 $Å^3$ containing 3929 electrons/cell. Assuming all the density in the solvent voids was from DEF molecules, this roughly translated to approximately 72 DEF molecules per cell. Both Site 1 and Site 2 locations have general site multiplicity of 48. Difference-Fourier maps suggested that Site 1 was higher in occupancy than Site 2. Hence, Site 1 was assumed to have a full DEF molecule, generating 48 DEF molecules in the unit cell. Site 2 was assumed to contain the remaining 24 DEF molecules to generate a half occupied solvent site location. Refinement of the structure after solvent modeling resulted in a significant drop in the residual error. While the final structure factors do not reflect the now absent DEF solvent, the final refinement included the additional DEF chemical species within the chemical formula and the reported crystal data reflect the presence of 1.5 DEF molecules per formula unit for the SMOF-1 structure.

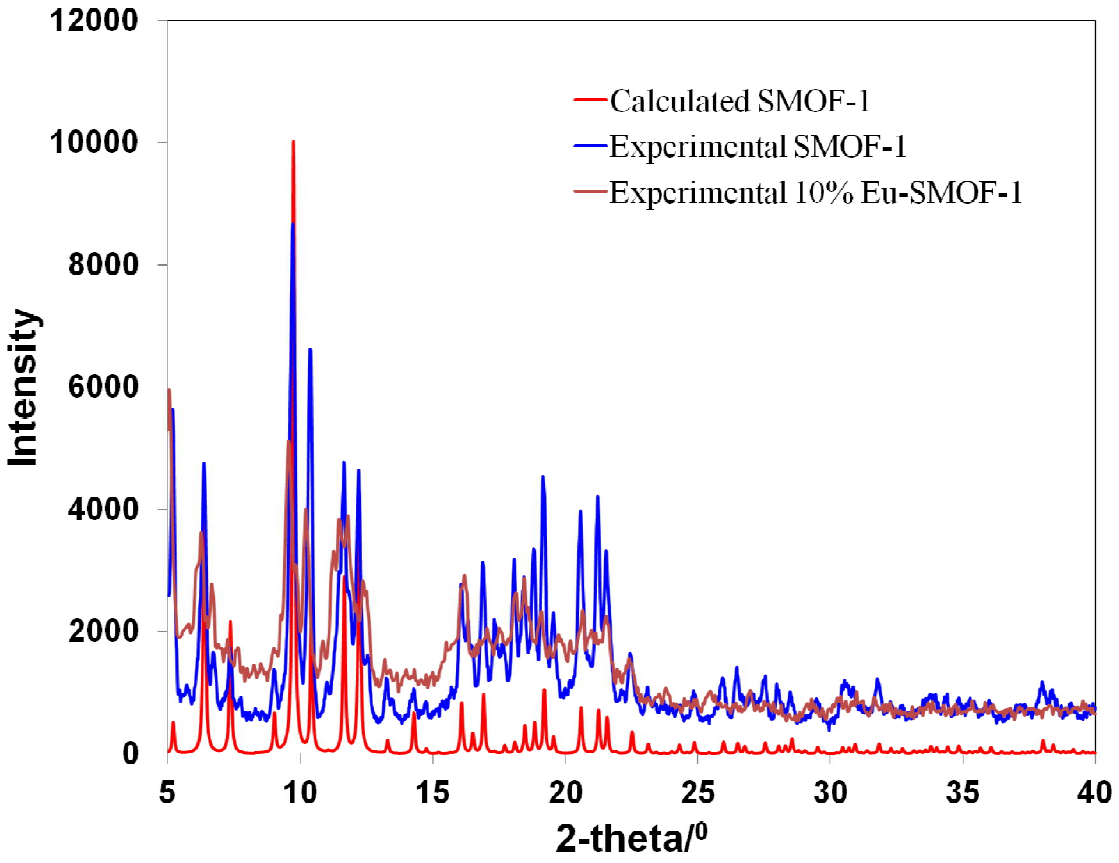
Table S1. Crystal data and structure refinement for **SMOF-1**.

Empirical formula	C20 H10 In O8, (C5 H11 O N)*1.5
Formula weight	644.82
Temperature	188 K
Wavelength	0.71073 Å
Crystal system, space group	cubic, Ia-3
Unit cell dimensions	a = 33.975(3) Å alpha = 90°
	b = 33.975(3) Å beta = 90°
	c = 33.975(3) Å gamma = 90°
Volume	39217(10) $Å^3$
Z, Calculated density	48, 1.002 Mg/m^3
F(000)	11664
Crystal size	0.21 x 0.21 x 0.23 mm
Theta range for data collection	5.61 to 38.39°
Reflections collected / unique	119137 / 4726 [R(int) = 0.062]
R indices (all data)	R1 =0.0691, wR2 = 0. 2664
Largest diff. peak and hole	0.62 and -0.28 $eÅ^{-3}$

Section S3: Powder X-Ray Diffraction (XRD) measurements

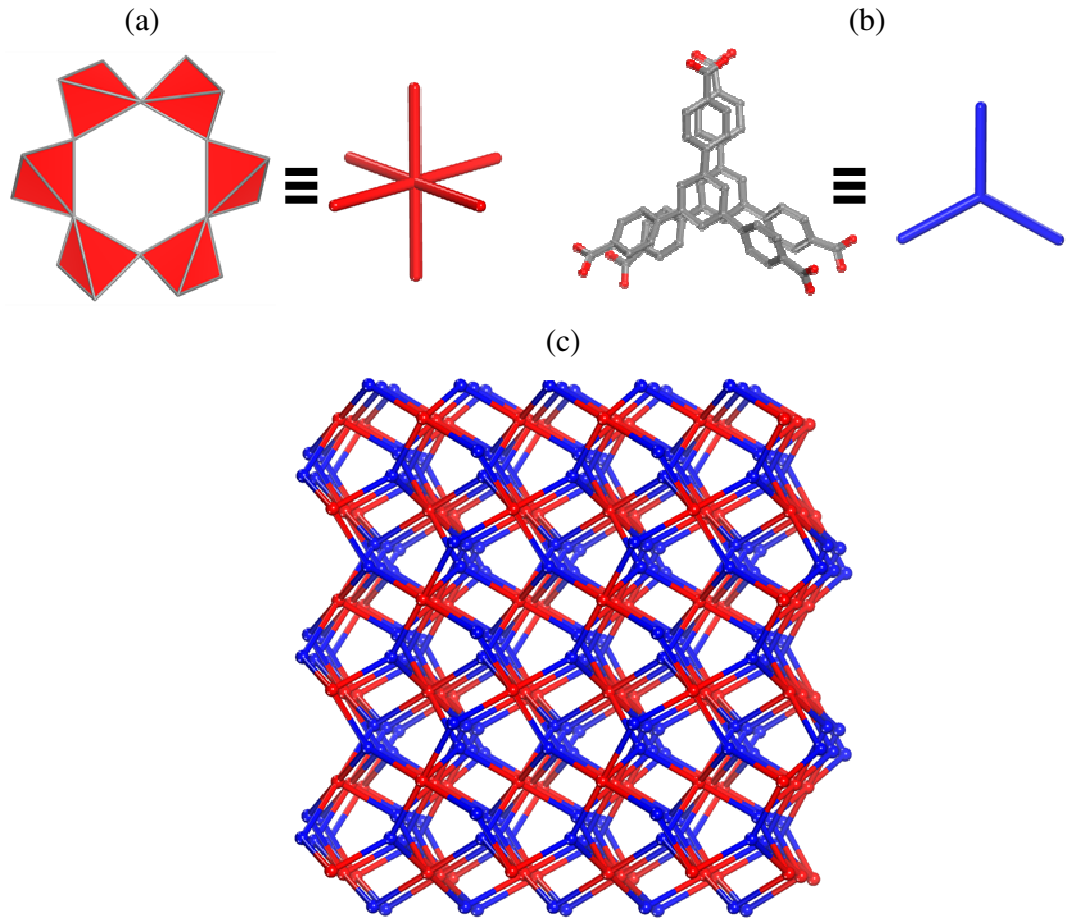
Powder X-Ray Diffraction (XRD) measurements were performed on a Siemens Kristalloflex D500 diffractometer, CuKα radiation (λ = 1.54178 Å).

Figure S1. XRD powder pattern on SMOF-1, indicating phase purity of the as-synthesized materials.



Section S4: Simplified topological evaluation

Figure S2. Simplified alternative topological analysis in SMOF-1, where (a) the 6-member ring corner sharing tetrahedra is viewed as a 6-connected node; (b) the two corrugated BTB linkers within a distinct net are simplified to a fused 3-connected point of extension; (c) the resulting (3,6)- connected pyrite (*pyr*) topology.



Section S5: Photoluminescence (PL) measurements

PL measurements

The PL emission and excitation spectra were collected using a Horiba Jobin-Yvon Fluorolog-3 double-grating/double-grating Fluorescence Spectrophotometer. Powders were deposited onto glass slides. PL emission and excitation measurements were made by orienting the samples 11° from the incident beam and detecting the emitted light from the front face of the sample. Excitation spectra were collected by monitoring at the peak of the emission, and scanning over UV wavelengths, e.g., 250-365 nm.

Figure S3. Unique arrangement of BTB linkers in SMOF-1.

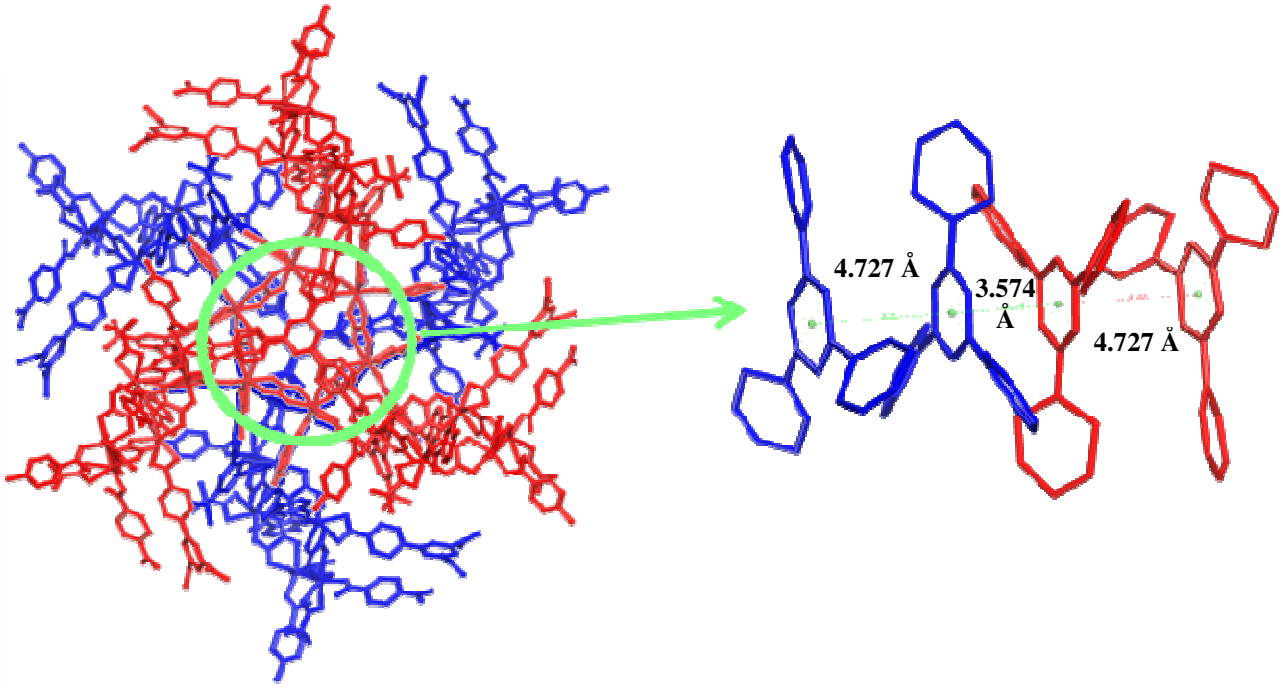


Figure S4. Excitation spectra in SMOF-1 and 10% Eu-SMOF-1.

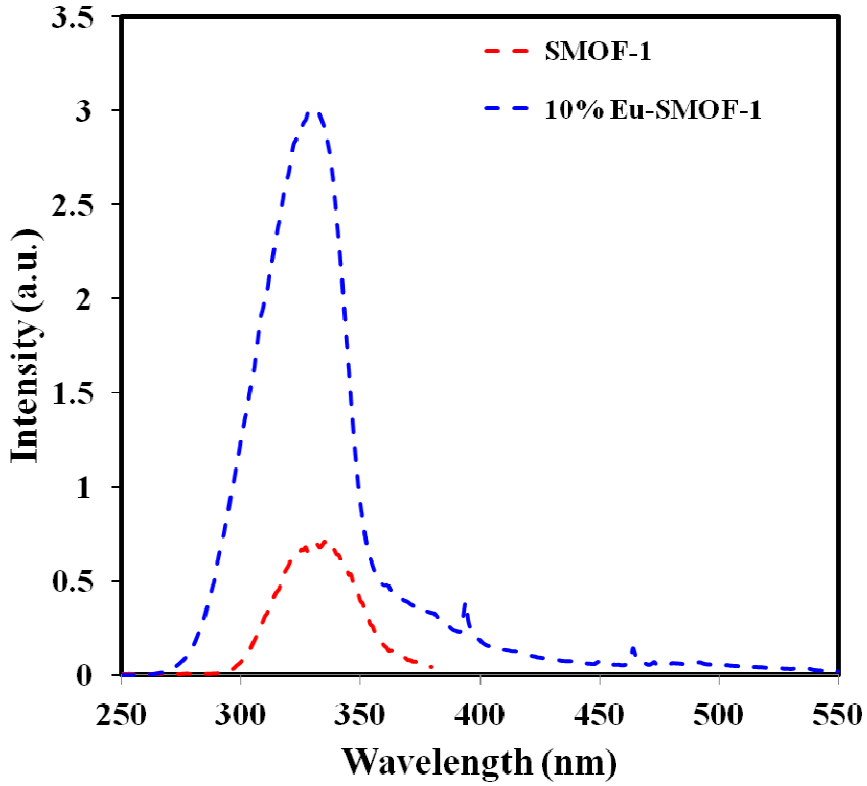


Table S2. Excitation spectra in SMOF-1 and 10% Eu-SMOF-1.

λ_{ex}	CRI		CCT (K)		x		y	
	SMOF-1	Eu-SMOF-1	SMOF-1	Eu-SMOF 1	SMOF-1	Eu-SMOF-1	SMOF-1	Eu-SMOF-1
330	77.4	45	34463	1410	0.209	0.512	0.193	0.298
350	84.5	63	22413	3606	0.241	0.369	0.268	0.301
360	85.1	81	33290	7068	0.234	0.309	0.275	0.298
380	81.1	93	21642	8695	0.235	0.285	0.387	0.309

Section S6: SEM-EDS analyses

Scanning Electron Microscopy (SEM) images were captured on a FEI NovaNano SEM 230, and Energy Dispersive Spectroscopy (EDS) analyses were collected on a EDAX Genesis Apex 2 with an Apollo SDD detector.

Figure S5. SEM images of single crystals of as-synthesized SMOF-1.

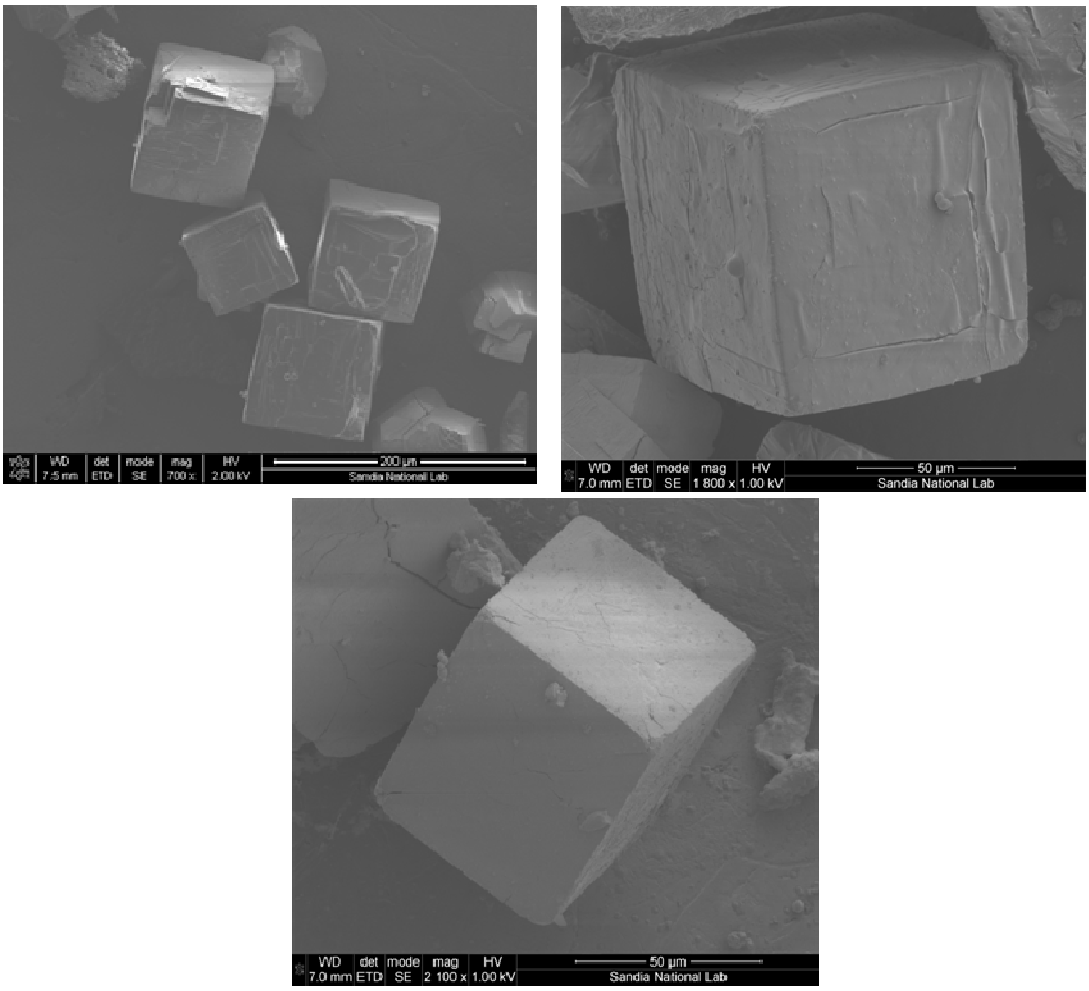
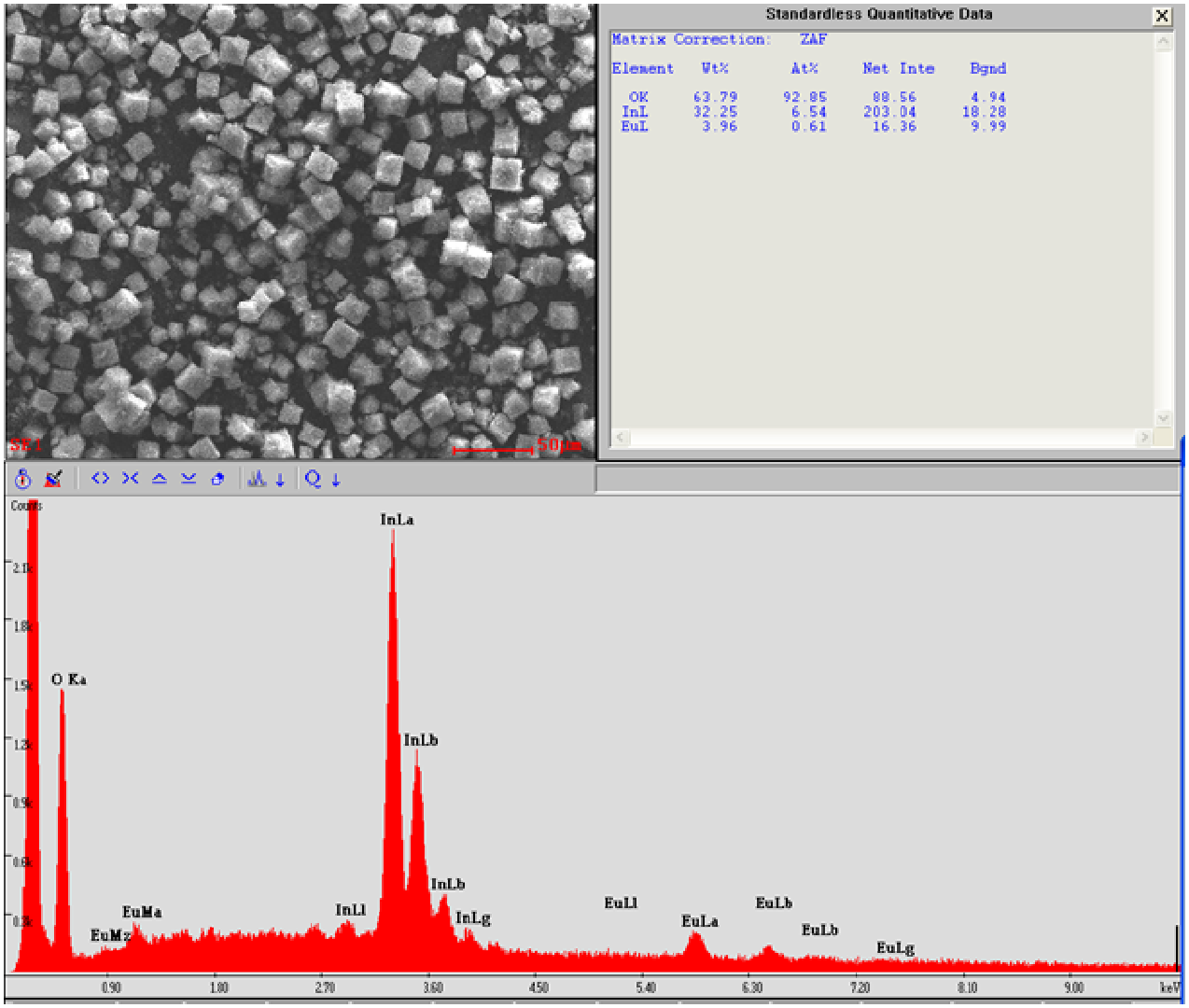
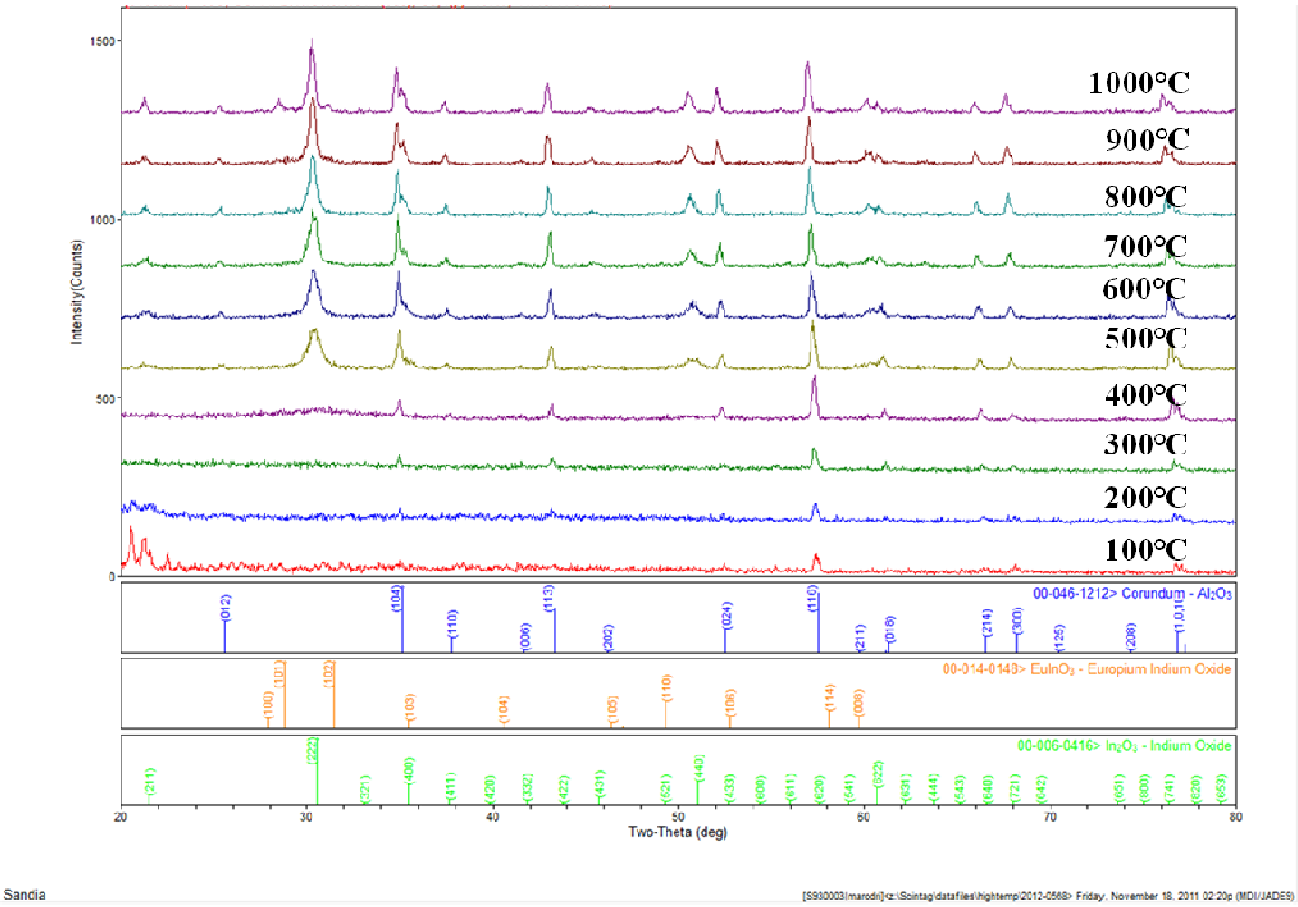


Figure S6. SEM-EDS analyses of 10% Eu-SMOF-1.



Section S7: *In situ* temperature programmed XRD measurements

Figure S7. *In situ* temperature programmed XRD measurements on the 10% Eu-SMOF-1 sample highlighting the formation of In_2O_3 and $EuInO_3$ above 400°C (Al_2O_3 peaks are associated with sample holder).

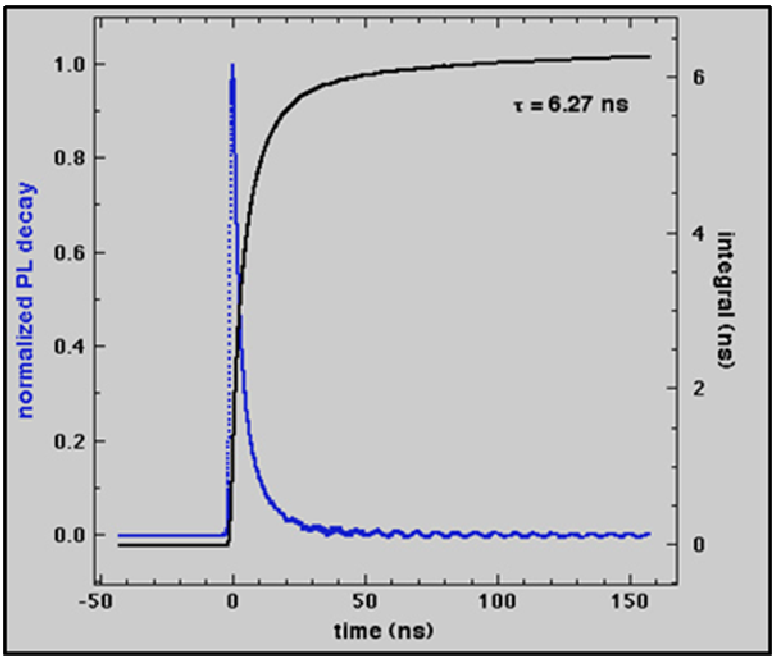


Section S8: PL lifetime measurements

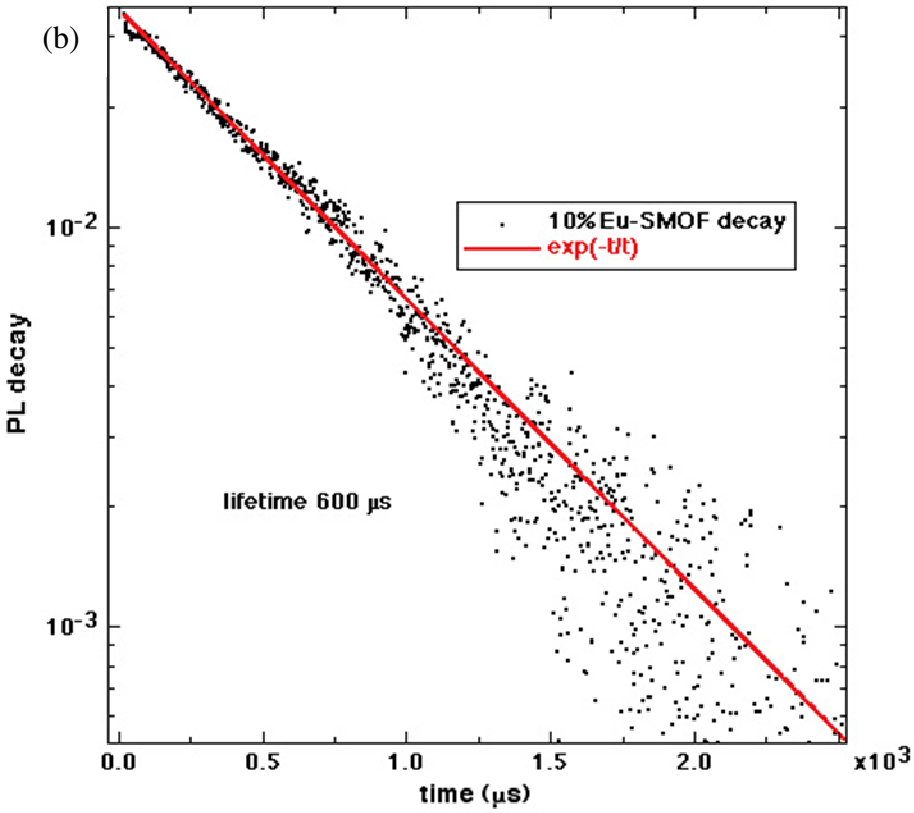
PL lifetime of the broadband emission was measured by exciting the pristine, dried solid powder with a PTI GL3300 pulsed nitrogen laser at 337 nm, pumping a GL301 dye laser with the output set to 380 nm. Two Thorlabs 210 silicon photodiode detectors with a response time less than 1 ns were used – one detector was used to trigger the scope, the other measured the emission. A UV-blocking interference filter was placed in front of the detector to block the excitation light. The signals were averaged using a 1 GHz Tektronix TDS5104 digital oscilloscope. The observed decay of the emission was slightly non-exponential, requiring the integration of the normalized decay curve to obtain the harmonic average lifetime, which was 6.27 ns. The PL lifetime of the 10% Eu-SMOF-1 emission was measured by exciting the doped powder with the pulsed nitrogen laser at 337 nm. Two Thorlabs PDA55 silicon photodiode detectors were used. The decay was single exponential with a lifetime of 600 microseconds. This long lifetime is due to the low oscillator strength of the 4f-4f transitions of Eu^{3+}.

Figure S8. PL lifetime measurements on (a) SMOF-1, (b) 10% Eu-SMOF-1.

(a)



(b)



Section S9: Thermogravimetric-mass spectrometry analyses

Thermal Gravimetric Analysis (TGA) and Mass Spectroscopy (MS) measurements were conducted on a SDTQ600 TA instrument, equipped with a mass-spectrometer gas analyzer MS-ThermoStar™ from Pfeiffer Vacuum. All samples were heated to 800 °C (1073 K) at a 5 °C/min. heating rate, under continuous nitrogen flow.

Figure S9. Overlays of thermogravimetric traces of as-synthesized (red), and the ethanol-exchanged sample (scan rate: 5°C/min), where the 23% initial mass loss is equivalent to the corresponding calculated DEF molecules present in the as synthesized SMOF-1, based on the formula unit.

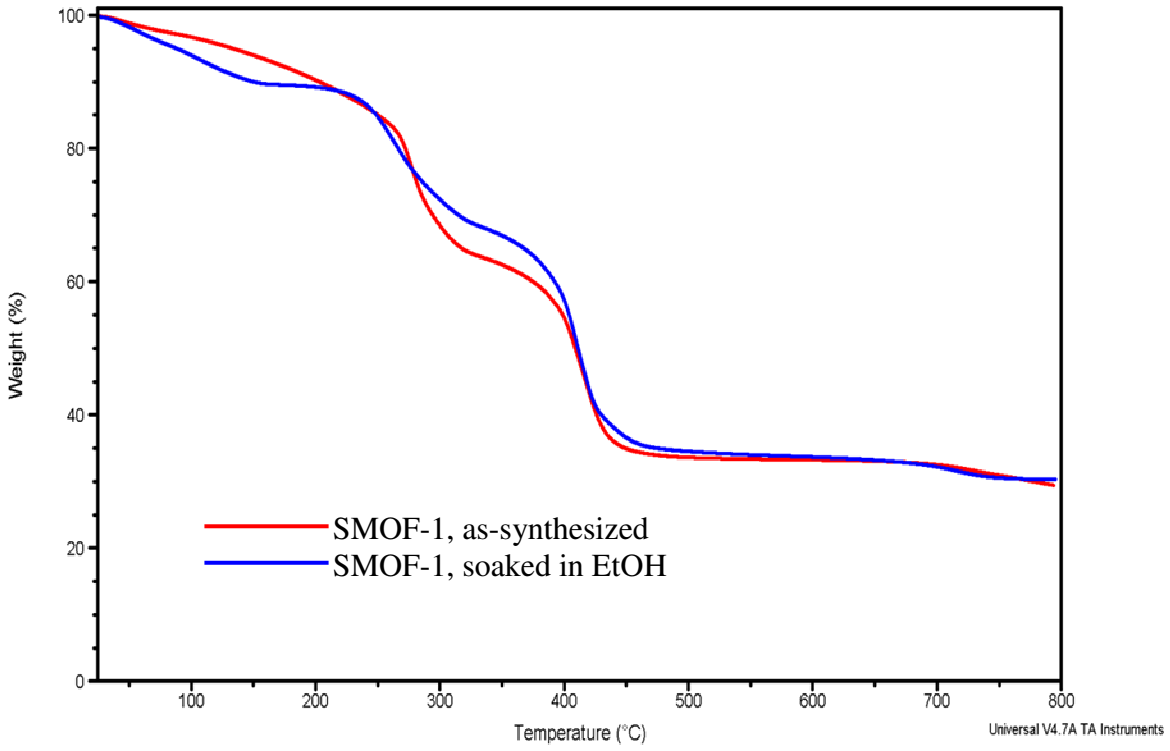
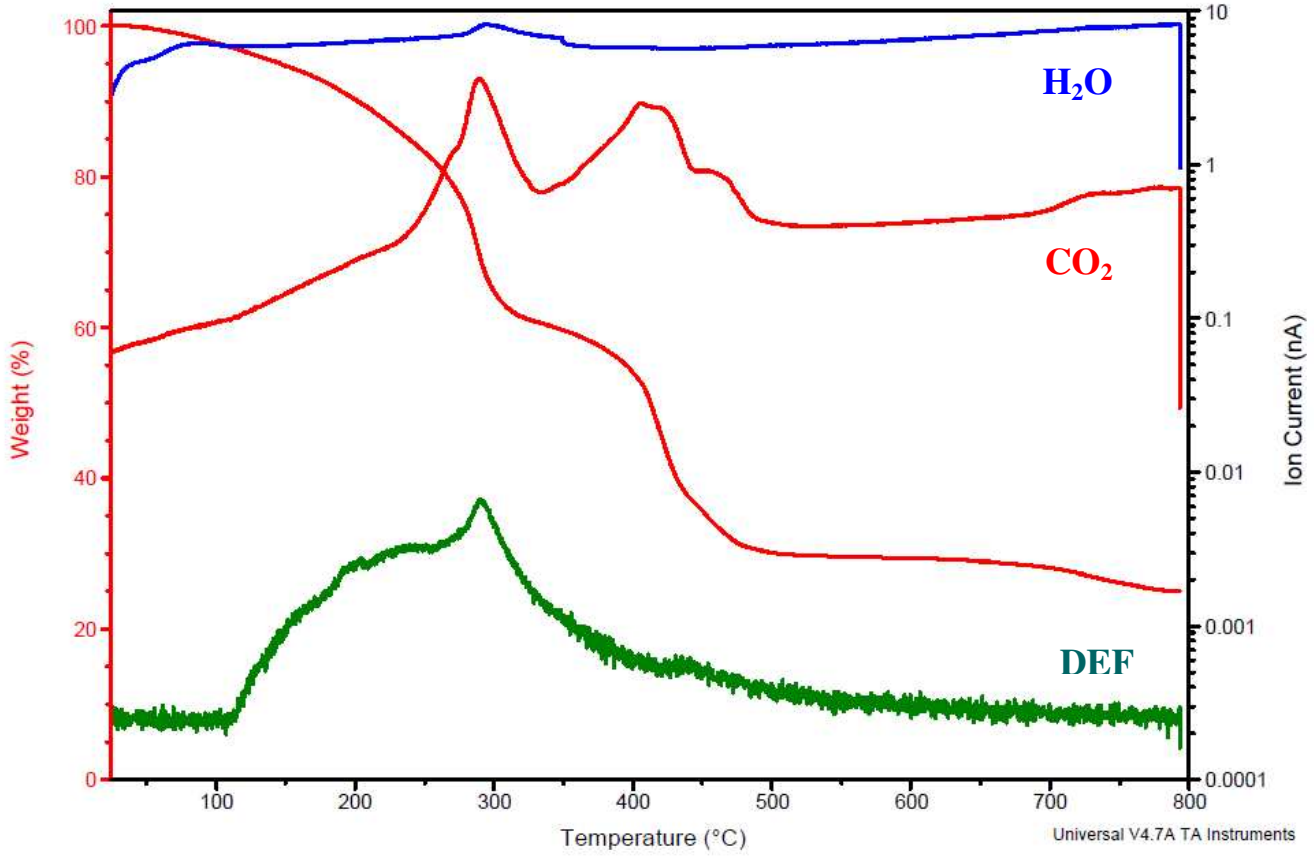


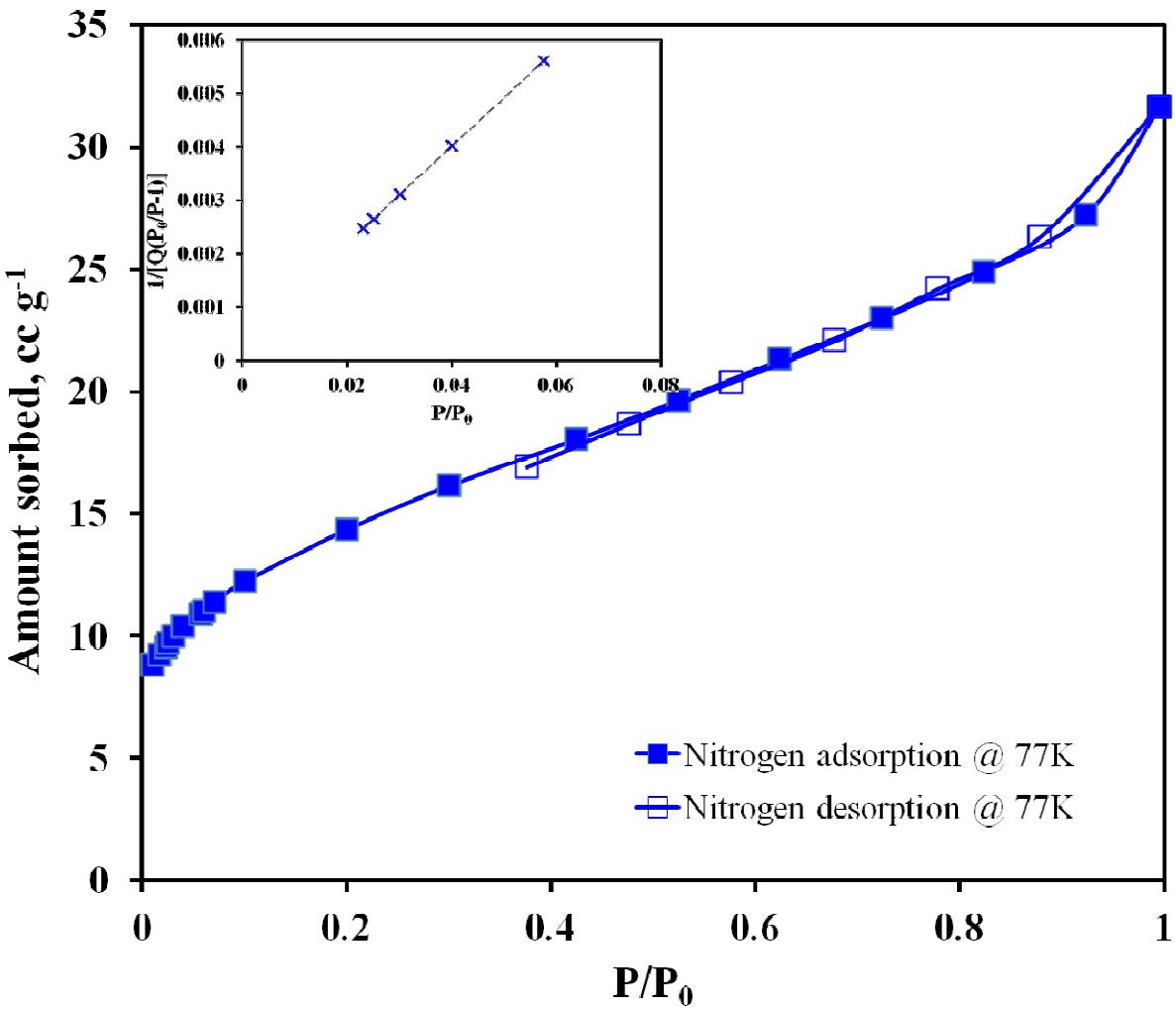
Figure S10. Thermogravimetric-mass spectrometer analyses of the as-synthesized SMOF-1 sample, monitoring the water (blue), carbon dioxide (red), and *N,N'*-diethylformamide (green) release upon gradual heating (scan rate: 10°C/min).



Section S10: Gas sorption measurements

Nitrogen adsorption isotherms were measured at 77K, using a Micromeritics ASAP 2020 surface area and porosity analyzer. Nitrogen of ultra-high purity 99.999% (Matheson Tri-Gas) was used in these experiments.

Figure S11. Nitrogen sorption isotherm at 77K; inset: BET surface area plot model; BET= 47 m^2/g.



Section S11: References

S1. Bruker AXS, Inc. **1998** *SMART* Version 5.054. Madison, WI 53711-5373.

S2. (a) Sheldrick, G. M. **2008** *Acta Cryst*., A64, 112-122; (b) Bruker AXS, Inc. **2000** *XSHELL* Version 4.01 and *SHELXTL* Version 6.10. Madison, WI 53711-5373.

S3. Spek, A. L. **2008** Platon, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands.