

# Near-UV photo-induced modification in isorecticular metal-organic frameworks

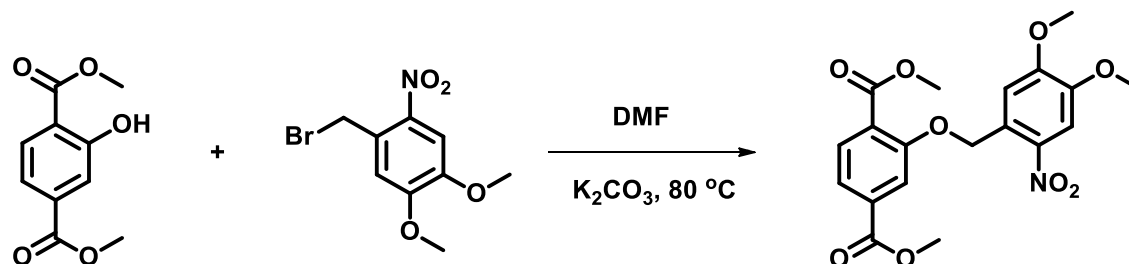
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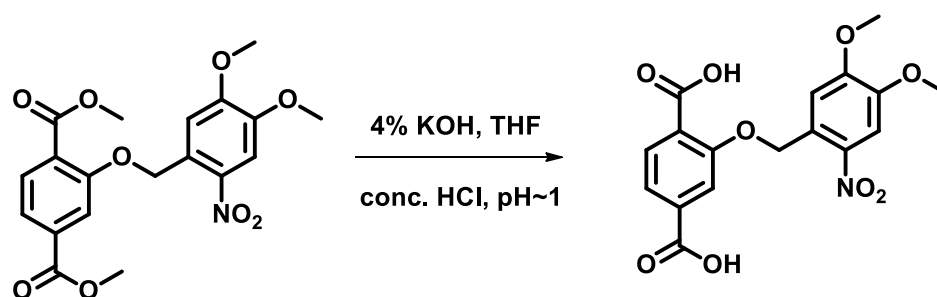
## **ELECTRONIC SUPPLEMENTARY INFORMATION**

## Experimental Section

*General.* Dimethyl-2-hydroxyterephthalate and 2-((2-nitrobenzyl)oxy)terephthalic acid were synthesized as previously reported (K. K. Tanabe, C. A. Allen and S. M. Cohen, *Angew. Chem. Int. Ed.*, 2010, **49**, 9730-9733).



*Dimethyl 2-((4,5-dimethoxy-2-nitrobenzyl)oxy)terephthalate.* Dimethyl-2-hydroxyterephthalate (1.2 g, 5.6 mmol) was dissolved in 60 mL of DMF. 4,5-Dimethoxy-2-nitrobenzyl bromide (2.0 g, 7.3 mmol) and K<sub>2</sub>CO<sub>3</sub> (1.5 g, 11.1 mmol) were added and the mixture was stirred at 80 °C for 1 h. While hot, the K<sub>2</sub>CO<sub>3</sub> was filtered off, and water was added to the filtrate to precipitate out the product. The pale yellow solid was isolated by vacuum filtration and washed with MeOH to remove any unreacted starting materials. Yield: 2.04 g (90%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 25 °C): δ 3.89 (s, 3H; CO<sub>2</sub>CH<sub>3</sub>), 3.97 (s, 3H; OCH<sub>3</sub>), 3.99 (s, 3H; OCH<sub>3</sub>), 4.13 (s, 3H; CO<sub>2</sub>CH<sub>3</sub>), 5.62 (s, 2H, CH<sub>2</sub>) 7.72 (d, 1H; ArH), 7.80 (s, 2H; ArH), 7.94 (d, 1H; ArH), 8.06 (s, 1H; ArH). ESI-MS(+): *m/z* 405.69[M+H]<sup>+</sup>, 427.98[M+Na]<sup>+</sup>.



*2-((4,5-dimethoxy-2-nitrobenzyl)oxy)terephthalic acid.* Dimethyl 2-((4,5-dimethoxy-2-nitrobenzyl)oxy)terephthalate (1.68 g, 4.1 mmol) was dissolved in 500 mL of THF followed by the addition of 4% KOH (aq) (250 mL). After stirring the solution at room temperature for 2 h, the solution was diluted with water (100 mL) and washed with diethyl ether twice (50 mL). The aqueous layer was collected and acidified to pH~1 using concentrated HCl to precipitate out a yellow solid. The solid was isolated via vacuum filtration, washed with H<sub>2</sub>O, and dried under vacuum at room temperature. Yield: 1.27 g (81%). <sup>1</sup>H NMR (*d*<sup>6</sup>-DMSO, 400 MHz, 25 °C): δ 3.88 (s, 3H; OCH<sub>3</sub>), 3.94 (s, 3H; OCH<sub>3</sub>), 5.58 (s, 2H, CH<sub>2</sub>) 7.61 (d, 1H; ArH), 7.69 (s, 1H; ArH), 7.75 (s, 1H; ArH), 7.88 (d, 2H; ArH). ESI-MS(-): *m/z* 375.85[M-H]<sup>-</sup>.

*IRMOF-1-OH Direct Synthesis Attempt.* Under identical conditions to IRMOF-1-L1 no solid material was obtained.

*IRMOF-1-(OH)(NH<sub>2</sub>) Direct Synthesis Attempt.* Under identical solvothermal conditions to IRMOF-1-(L1)(NH<sub>2</sub>), using varying ratios of NH<sub>2</sub>-BDC to HO-BDC, no solids were obtained that incorporated both ligands in either DMF or DEF.

## Characterization

*<sup>1</sup>H NMR analysis.* Approximately 5 mg of MOF was dried under vacuum at 100 °C (or used immediately after BET analysis) and digested in 500 μL of *d*<sup>6</sup>-DMSO and 100 μL of dilute DCl (23 μL of 35% DCl in D<sub>2</sub>O diluted with 1.0 mL of *d*<sup>6</sup>-DMSO). All percentages of PSD are reported from two independent samples.

*Analysis by ESI-MS.* Samples for analysis were prepared by taking 10 μL of <sup>1</sup>H NMR solution diluted with 1 mL MeOH.

*Thermal Analysis.* Approximately 10-20 mg of MOF (following BET analysis) was used for these measurements. Samples were analyzed under a dinitrogen stream from room temperature to 600 °C at 5 °C/min.

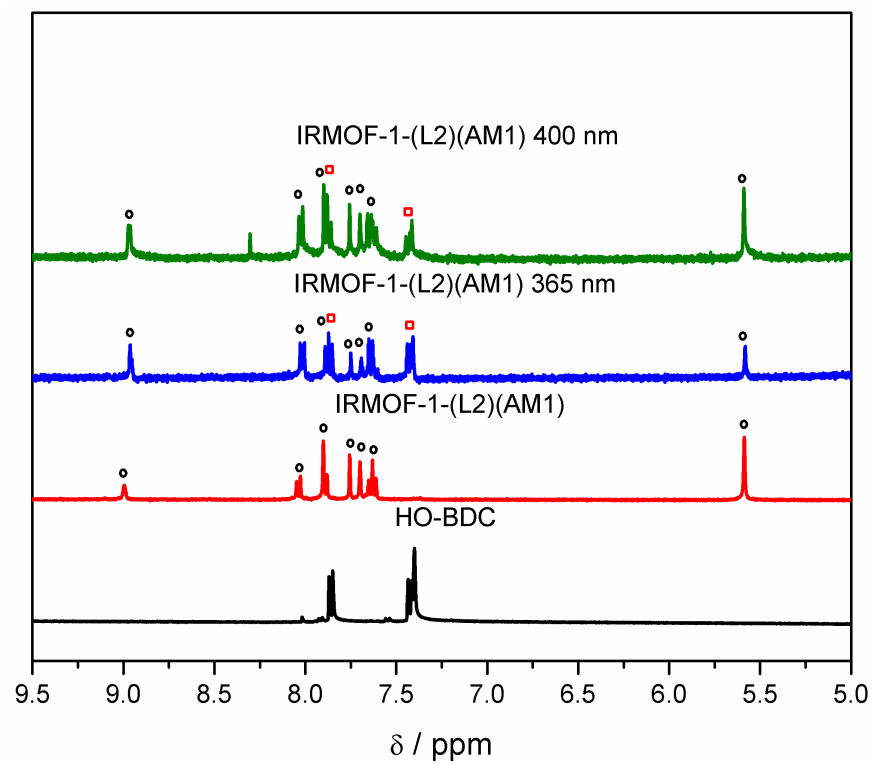
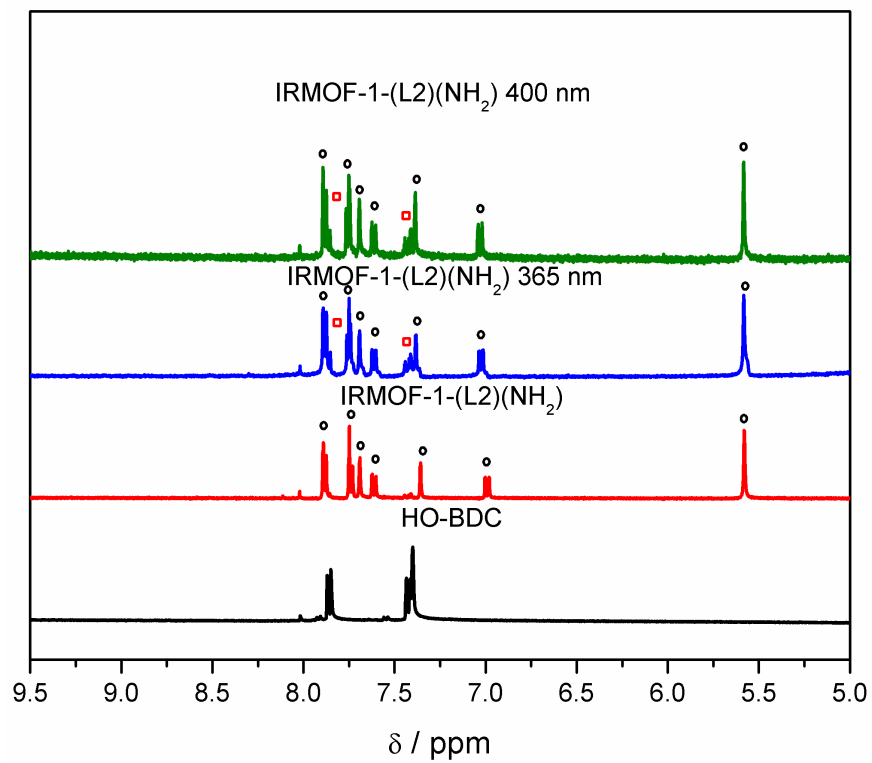
*PXRD Analysis.* Approximately 15 mg of MOF (soaked in DMF) was air dried prior to PXRD analysis. Powder X-ray diffraction (PXRD) data were collected at ambient temperature with a scan speed of 0.5 sec/step, step size of 0.02° in 2θ, and a 2θ range of 3-40 °.

*BET Surface Area Analysis.* Approximately 60-100 mg of MOF (previously in CHCl<sub>3</sub>) was evacuated on a vacuum line for <1 min at RT. The sample was transferred to a preweighed sample tube and degassed at 105 °C (25 °C for L2 containing samples) for a minimum of 12 h or until the outgas rate was < 5 μmHg. The sample tube was re-weighed to obtain a consistent sample mass. BET surface area (m<sup>2</sup>/g) measurements were collected on at least three independent samples of each MOF at 77 K by dinitrogen using the volumetric technique.

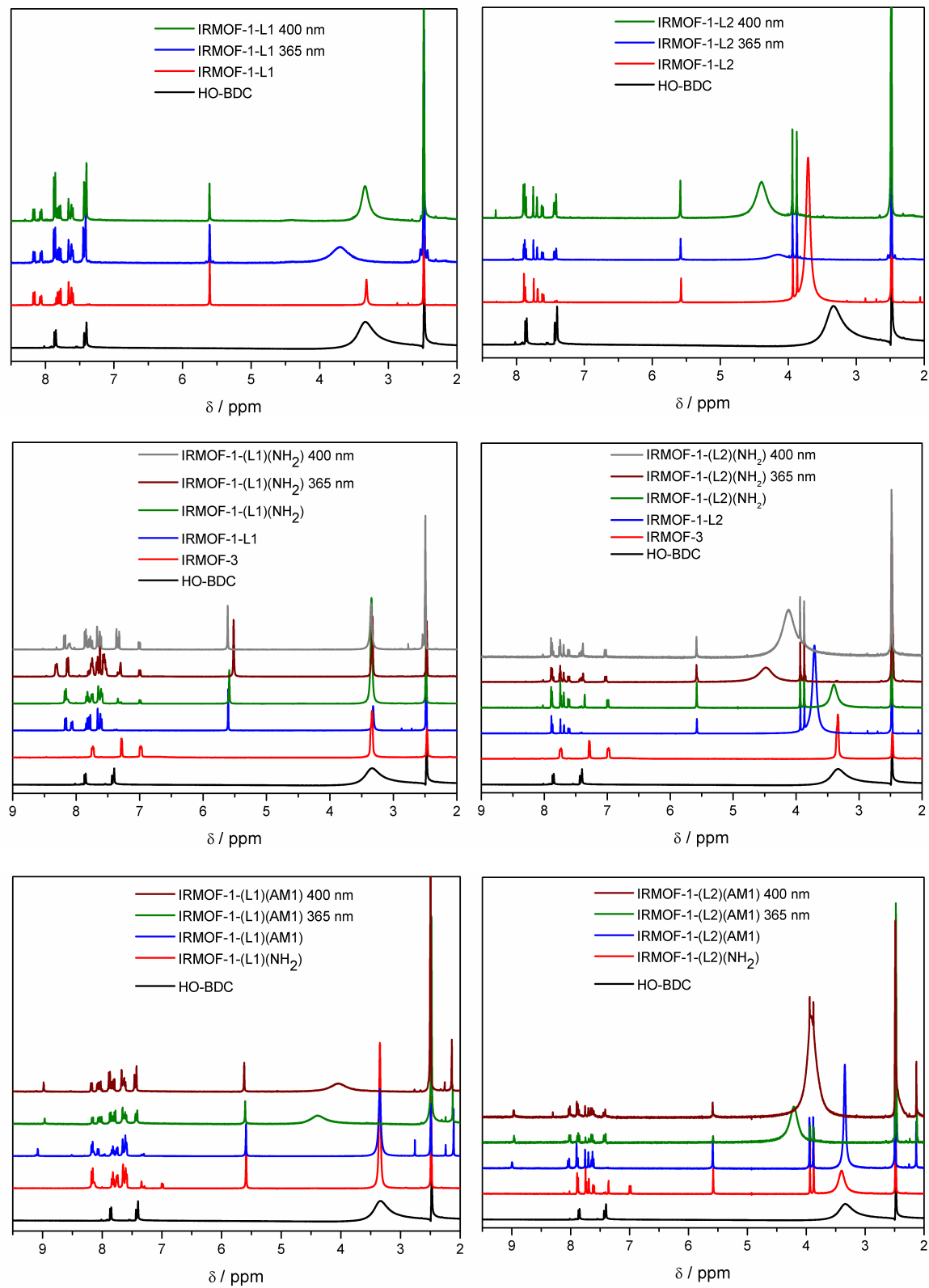
*Single Crystal X-ray Diffraction.* Single crystals of IRMOF-1-L1, IRMOF-1-L1 after being exposed to 365 nm for 48h, IRMOF-1-L2, and IRMOF-1-(L1)(NH<sub>2</sub>) were mounted on nylon loops with Paratone oil and placed under a nitrogen cold stream (200 K). A semiempirical method utilizing equivalents was employed to correct for absorption. All data collections were solved and refined using SHELXTL and treated with the “squeeze” protocol in PLATON to account for electron density associated with the nitrobenzyl groups and disordered solvent molecules within the framework.

*Solid State UV-Vis analysis.* Approximately 15 mg of IRMOF (soaked in CHCl<sub>3</sub>) was air dried for UV-Vis analysis.

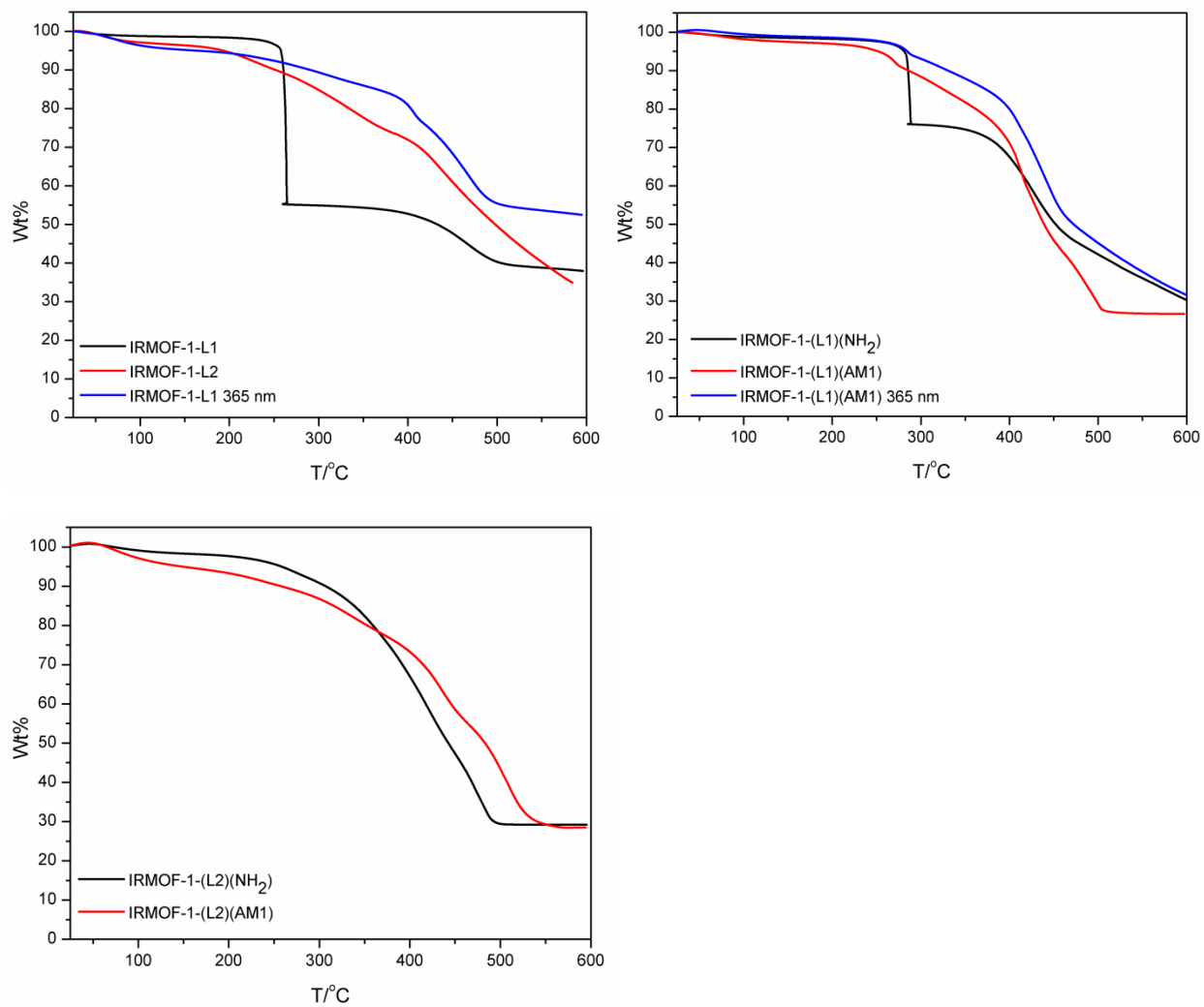
*UV-Vis Spectroscopy.* Absorption spectra of a 1.0 mL solution of methyl diester form of the ligands was prepared at 50 μM concentration in EtOAc and spectra were collected at room temperature.



**Fig. S1** <sup>1</sup>H NMR comparison of IRMOF-1-(L2)(NH<sub>2</sub>) and IRMOF-1-(L2)(AM1) before and after PSD at 365 nm or 400 nm.



**Fig. S2** Complete  $^1\text{H}$  NMR spectra of IRMOFs before and after PSD at 365 nm or 400 nm.



**Fig. S3** TGA traces of IRMOFs.

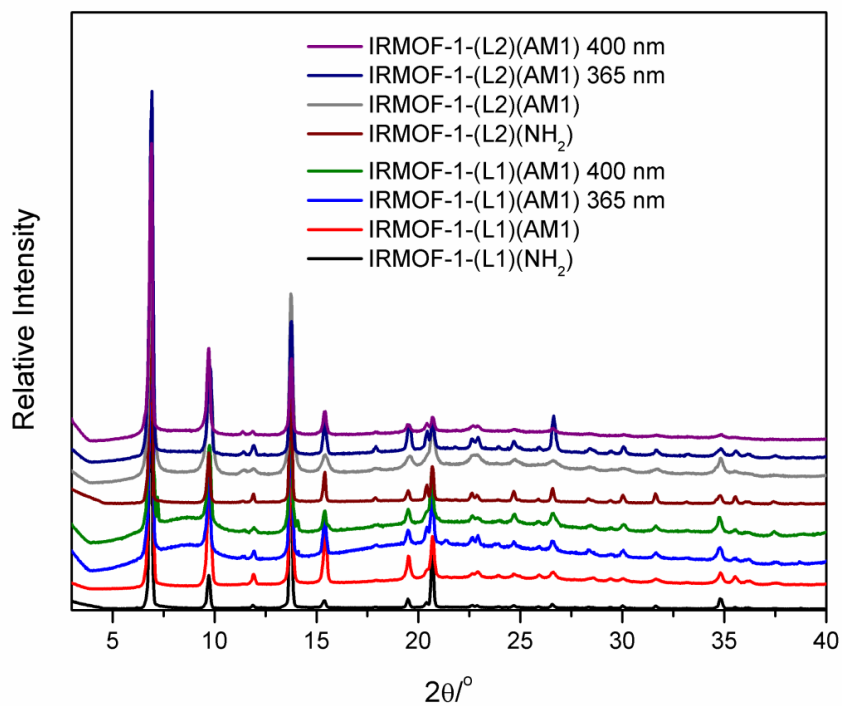


Fig. S4 PXR D spectra of IRMOFs.

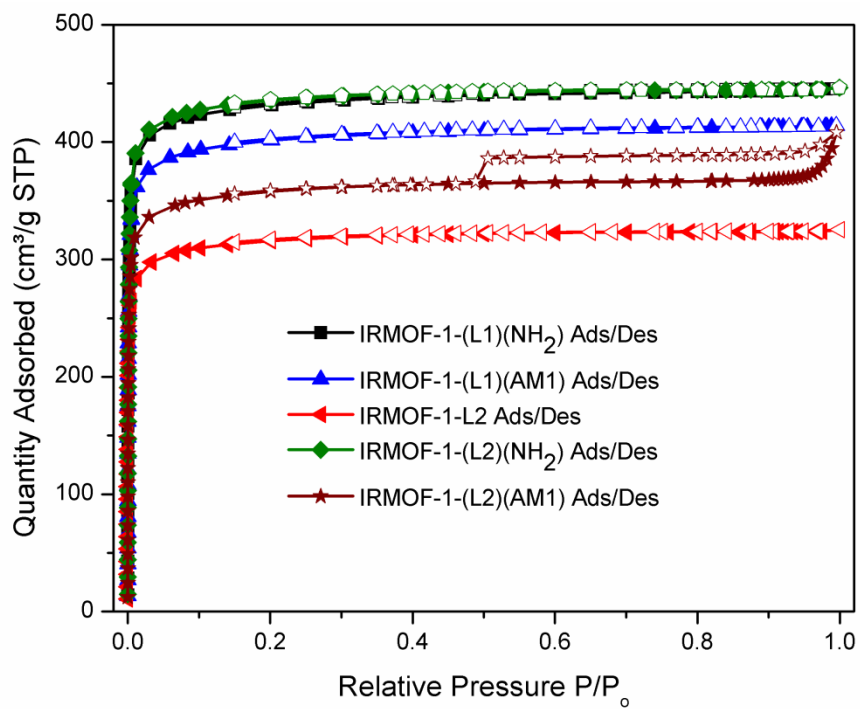
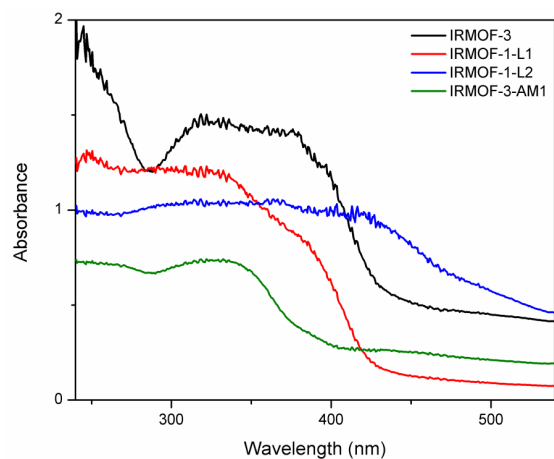
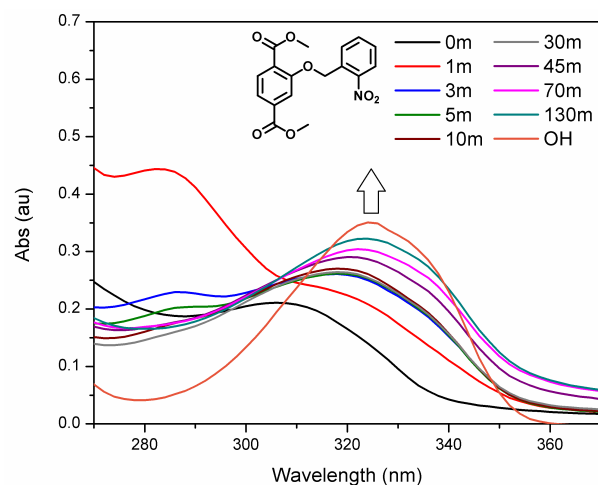


Fig. S5 Dinitrogen isotherms of IRMOFs prior to PSD.

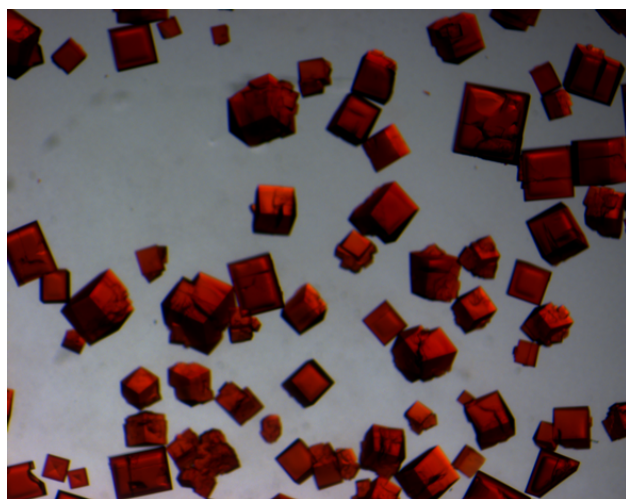
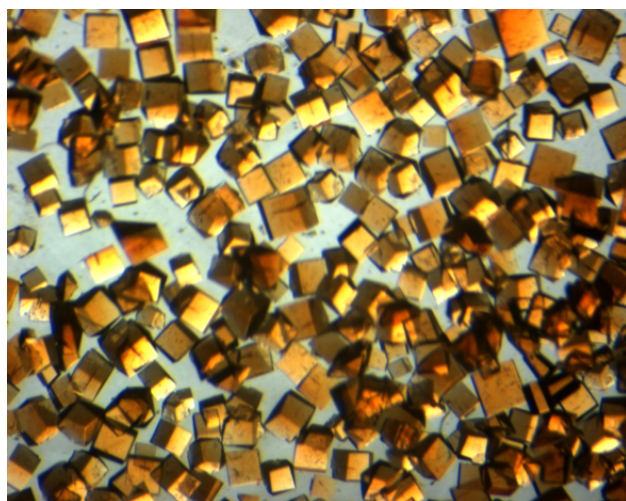
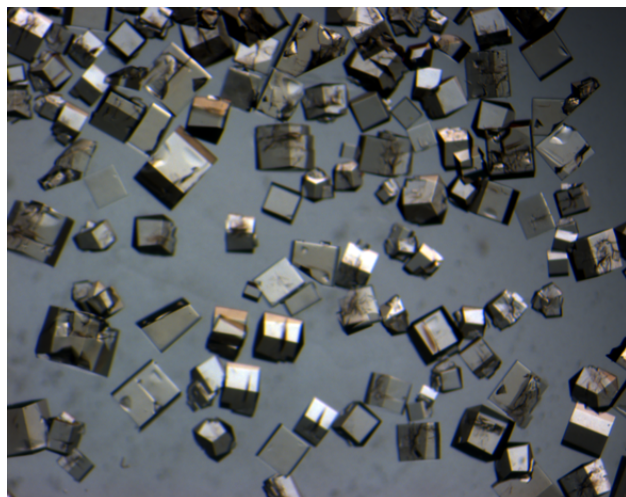


**Fig. S6** Solid state UV-Vis spectra of IRMOFs.

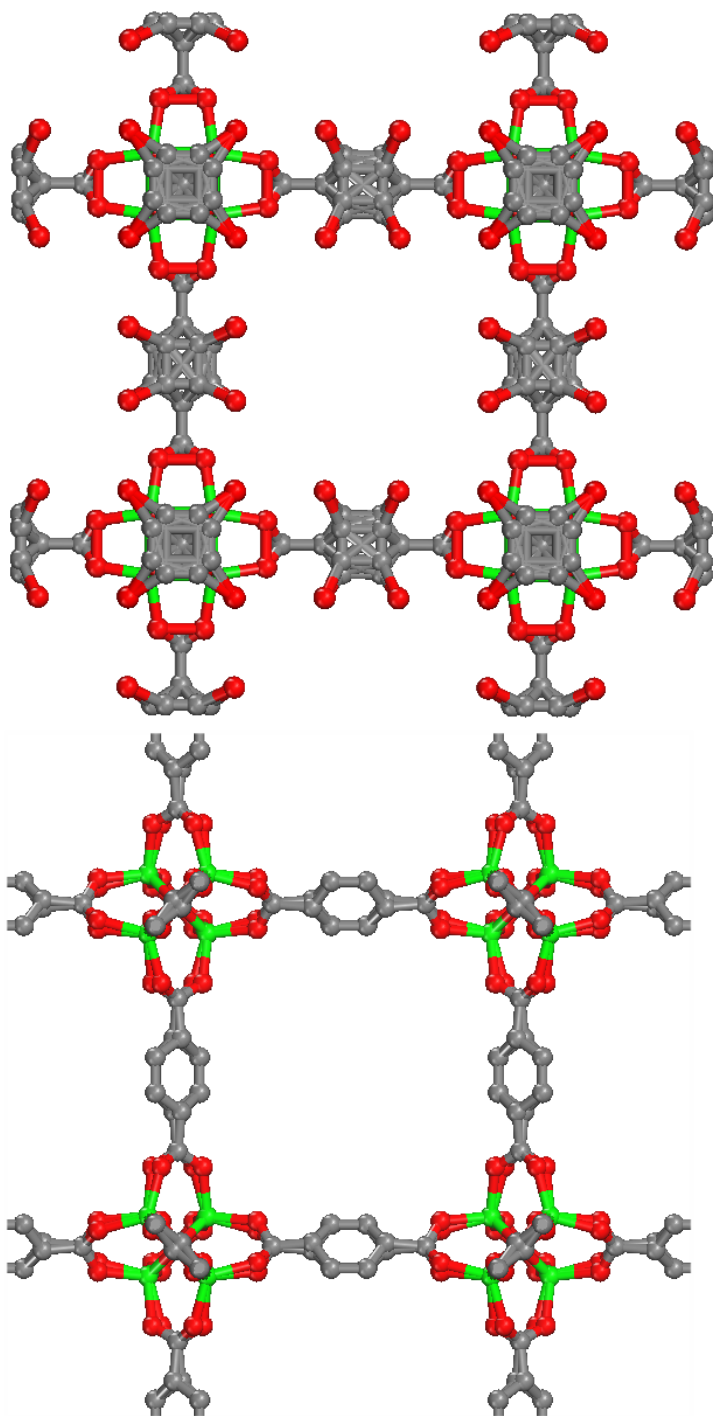


**Fig. S7** Solution UV-Vis spectra of esterified L1 irradiated at 365 nm. The increase at 288 nm is due to the liberated nitrosobenzaldehyde that undergoes photodecomposition upon prolonged exposure to light (M. Gaplovsky, Y. V. Il'ichev, Y. Kamdzhilov, S. V. Kombarova, M. Mac, M. A. Schworer and J. Wirz, *Photochem. Photobiol. Sci.*, 2005, **4**, 33-42). A clean isosbestic point is not observed due to various byproducts of the PSD reaction.





**Fig. S8** Photographs of crystals of IRMOF-1-L1 (top), IRMOF-1-L2 (middle), and IRMOF-1-OH (bottom) generated from IRMOF-1-L1 after irradiation at 365 nm.



**Fig. S9** X-ray crystal structure for IRMOF-1-L1 before (top) and after (bottom) PSD at 365 nm. While the structure of IRMOF-1-L1 possesses some significant disorder and is found in a different space group than many IRMOF crystals, the structure obtained and powder pattern confirm the expected IRMOF topology.

**Table S1.** Crystal data and structure refinement for IRMOF-1-L1.

Identification code	IRMOF-1-L1
Empirical formula	C <sub>45</sub> H <sub>21</sub> N <sub>3</sub> O <sub>22</sub> Zn <sub>4</sub>
Formula weight	1210.78
Temperature	200 (2) K
Wavelength	0.71073 Å
Crystal system	Cubic
Space group	<i>Pm-3m</i>
Unit cell dimensions	$a = 12.8489(12) \text{ \AA}$ $\alpha = 90^\circ$ $b = 12.8489(12) \text{ \AA}$ $\beta = 90^\circ$ $c = 12.8489(12) \text{ \AA}$ $\gamma = 90^\circ$
Volume	2121.3(3) Å <sup>3</sup>
Z	2
Density (calculated)	1.587 Mg/m <sup>3</sup>
Absorption coefficient	2.318 mm <sup>-1</sup>
F(000)	992
Crystal size	0.50 x 0.50 x 0.10 mm <sup>3</sup>
Theta range for data collection	1.58 to 25.26°.
Index ranges	-15 ≤ h ≤ 13, -15 ≤ k ≤ 15, -15 ≤ l ≤ 15
Reflections collected	12150
Independent reflections	446 [R(int) = 0.0419]
Completeness to theta = 25.26°	100.0 %
Max. and min. transmission	0.5431 and 0.3903
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	446 / 1 / 32
Goodness-of-fit on F <sup>2</sup>	1.644
Final R indices [I > 2σ(I)]	R1 = 0.1116, wR2 = 0.3415
R indices (all data)	R1 = 0.1173, wR2 = 0.3490
Largest diff. peak and hole	1.452 and -1.516 e.Å <sup>-3</sup>

**Table S2** Crystal data and structure refinement for IRMOF-1-OH, generated by irradiation of IRMOF-1-L1 at 365 nm.

Identification code	IRMOF-1-OH
Empirical formula	C <sub>24</sub> H O <sub>16</sub> Zn <sub>4</sub>
Formula weight	811.73
Temperature	200 K
Wavelength	0.71073 Å
Crystal system	Cubic
Space group	<i>Fm-3m</i>
Unit cell dimensions	$a = 25.8059(14) \text{ \AA}$ $\alpha = 90^\circ$ . $b = 25.8059(14) \text{ \AA}$ $\beta = 90^\circ$ . $c = 25.8059(14) \text{ \AA}$ $\gamma = 90^\circ$ .
Volume	17185.3(16) Å <sup>3</sup>
Z	16
Density (calculated)	0.586 Mg/m <sup>3</sup>
Absorption coefficient	1.124 mm <sup>-1</sup>
F(000)	2944
Crystal size	0.50 x 0.50 x 0.30 mm <sup>3</sup>
Theta range for data collection	1.37 to 25.37°
Index ranges	-31 ≤ h ≤ 31, -31 ≤ k ≤ 31, -29 ≤ l ≤ 29
Reflections collected	22285
Independent reflections	850 [R(int) = 0.0342]
Completeness to theta = 25.37°	100.0 %
Max. and min. transmission	0.7292 and 0.6035
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	850 / 0 / 30
Goodness-of-fit on F <sup>2</sup>	1.124
Final R indices [I > 2σ(I)]	R1 = 0.0925, wR2 = 0.2435
R indices (all data)	R1 = 0.0966, wR2 = 0.2557
Largest diff. peak and hole	5.055 and -0.951 e.Å <sup>-3</sup>

**Table S3.** Crystal data and structure refinement for IRMOF-1-L2.

Identification code	IRMOF-1-L2
Empirical formula	C <sub>51</sub> H <sub>39</sub> N <sub>2</sub> O <sub>28</sub> Zn <sub>4</sub>
Formula weight	1396.89
Temperature	200 (2) K
Wavelength	0.71073 Å
Crystal system	Cubic
Space group	<i>Fm-3m</i>
Unit cell dimensions	$a = 25.686(3) \text{ \AA}$ $\alpha = 90^\circ$ . $b = 25.686(3) \text{ \AA}$ $\beta = 90^\circ$ . $c = 25.686(3) \text{ \AA}$ $\gamma = 90^\circ$ .
Volume	16947(4) Å <sup>3</sup>
Z	16
Density (calculated)	0.594 Mg/m <sup>3</sup>
Absorption coefficient	1.139 mm <sup>-1</sup>
F(000)	2944
Crystal size	0.35 x 0.35 x 0.20 mm <sup>3</sup>
Theta range for data collection	1.37 to 25.31°.
Index ranges	-23 ≤ h ≤ 30, -30 ≤ k ≤ 10, - 27 ≤ l ≤ 21
Reflections collected	8788
Independent reflections	836 [R(int) = 0.0458]
Completeness to theta = 25.31°	100.0 %
Max. and min. transmission	0.8042 and 0.6912
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	836 / 0 / 25
Goodness-of-fit on F <sup>2</sup>	1.094
Final R indices [I > 2σ(I)]	R1 = 0.0650, wR2 = 0.1811
R indices (all data)	R1 = 0.0827, wR2 = 0.1989
Largest diff. peak and hole	1.075 and -0.398 e.Å <sup>-3</sup>

**Table S4.** Crystal data and structure refinement for IRMOF-1-(L1)(NH<sub>2</sub>).

Identification code	IRMOF-1-(L1)(NH <sub>2</sub> )
Empirical formula	C <sub>38</sub> H <sub>23</sub> N <sub>3</sub> O <sub>19</sub> Zn <sub>4</sub>
Formula weight	1080.81
Temperature	200(2) K
Wavelength	0.71073 Å
Crystal system	Cubic
Space group	<i>Fm-3m</i>
Unit cell dimensions	$a = 25.545(14) \text{ \AA}$ $\alpha = 90^\circ$ . $b = 25.545(14) \text{ \AA}$ $\beta = 90^\circ$ . $c = 25.545(14) \text{ \AA}$ $\gamma = 90^\circ$ .
Volume	16669(16) Å <sup>3</sup>
Z	16
Density (calculated)	0.604 Mg/m <sup>3</sup>
Absorption coefficient	1.158 mm <sup>-1</sup>
F(000)	2944
Crystal size	0.50 x 0.50 x 0.30 mm <sup>3</sup>
Theta range for data collection	1.59 to 25.70°.
Index ranges	-31 ≤ h ≤ 31, -31 ≤ k ≤ 30, - 28 ≤ l ≤ 30
Reflections collected	34575
Independent reflections	861 [R(int) = 0.0558]
Completeness to theta = 25.70°	99.9 %
Max. and min. transmission	0.7226 and 0.5951
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	861 / 0 / 14
Goodness-of-fit on F <sup>2</sup>	2.099
Final R indices [I > 2σ(I)]	R1 = 0.1774, wR2 = 0.4137
R indices (all data)	R1 = 0.2051, wR2 = 0.4524
Largest diff. peak and hole	2.072 and -1.050 e.Å <sup>-3</sup>