Electronic Supplementary Material (ESI) for ChemComm.

SUPPORTING INFORMATION

Alkaline-Earth Phosphonate MOFs with Hydration-Dependent Fluorescence

Zohreh Hassanzadeh Fard,[a] Yarry Kalinovskyy,[b] Denis Spasyuk,[c] Barry A. Blight*[b] and George K. H. Shimizu*[a]

[a] Department of Chemistry, University of Calgary, Calgary, Alberta T2N 1N4, Canada
Email: gshimizu@ucalgary.ca
[b] School of Physical Science, University of Kent, Canterbury, Kent, UK, CT6 6BF
Email: b.blight@kent.ac.uk

Experimental Details

Synthesis.

Starting materials:
4-bromobenzaldehyde, 4-bromoacetophenone, ammonium acetate, glacial acetic acid, 1,3-diisopropylbenzene, triethylphosphate, Nickel bromide, Hydrobromic acid (48%), Barium bromide, and Strontium hydroxide were used as received, without further purifications.

Synthesis of 2,4,6 tris(4-bromophenyl)pyridine: This starting material was prepared based on the modified reported method.[1] A mixture of 4-bromobenzaldehyde (3.00g, 16.20mmol), 4-bromoacetophenone (6.45g, 32.40mmol), CH_3COONH_4 (87.39g), and glacial acetic acid (45mL) was refluxed at 127°C overnight under Ar atmosphere. After cooling at~4◦C the precipitate was filtered, washed with acetic acid 50%, then with water. Cold acetone was added and the yellow solution pipette out in order to get the product as pure white solid (3.0 g, 34%).

Synthesis of 2,4,6 tris(4-diethylphosphonophenyl)pyridine: Synthesis followed by a modified Michaelis-Arbuzov reaction. 2,4,6-tris(4-bromophenyl)pyridine (3.00 g, 5.51 mmol) was added to 25 mL of diisopropylbenzene containing nickel (II) bromide (627.18 mg, 2.86 mmol) in a two-neck round bottom flask. The round bottom flask was equipped with a condenser and an addition funnel with a needle valve. The reaction was placed under inert Ar atmosphere and the diisopropylbenzene brought to reflux for 2 hours. Triethylphosphite (5.67 mL, 33.06 mmol) was mixed with 20.0 mL of diisopropylbenzene and added dropwise to the reaction over 2 hours. The reaction was allowed to reflux for 24 hours before cooling to room temperature. The resulting dark black solution was filtered to remove solid nickel (II) bromide and vacuum distilled to remove diisopropylbenzene and excess triethylphosphite. The result was viscous yellow oil was then directly used in the next step (3.19 g, 81% yield).
^{1}H NMR (400 MHz, CD_3OD): 8.45 (dd, 4H, Ar-H), 8.26.(s, 2H, Py-H), 8.09 (dd, 2H, Ar-H), 7.96 (m, 6H, Ar-H), 4.18 (m, 12H, methylene-H), 1.37 (t, 18H, methyl-H).
^{31}P{1H} NMR (162 MHz, CD_3OD): 18.95, 18.49.

Synthesis of 2,4,6 tris(4-phosphonophenyl)pyridine (H_6L): The diethyl ester was hydrolyzed using neat HBr. After 24 hour reflux the corresponding phosphonic acid precipitated as a white powder. Product was filtered and washed with water and methanol. It was air dried (82% yield).
^{1}H NMR (400 MHz, DMSO-d_6): 8.42 (dd, 4H, Ar-H), 8.34 (s, 2H, Py-H), 8.15 (dd, 2H, Ar-H), 7.87 (q, 6H, Ar-H).
^{13}C NMR (400 MHz, DMSO-d_6): 156.53 (S, 2C, Py-C2,6), 149.51 (S, 1C, Py-C4), 141.16 (S, 2C, Ar-C4), 140.09 (S, 1C, Ar-C4), 136.34, 134.56 (d, J_1:180Hz, 2C, Ar-C1), 136.49, 134.71 (d, J_1: 180Hz,

1C, Ar-C1), 131.70 (d, 2C, Ar-C2,6), 131.40 (d, 4C, Ar-C2,6), 127.59 (d, 2C, Ar-C3,5), 127.07 (d, 4C, Ar-C3,5), 118.08 (S, 2C, Py-C3,5).
$^{31}P\{1H\}$ NMR (162 MHz, DMSO-*d*$_6$): 12.36, 12.06
ESI-MS (80.0 V): m/z: 548.0411 $(M+H)^+$.

*Synthesis of anhydrous MOF **I***: $BaBr_2.2H_2O$ (98.03 mg, 0.296 mmol) was dissolved in 3 mL water. H_6L (81 mg, 0.148 mmol) was placed into a 23 mL Teflon-liner Parr autoclave. 4 mL DMF and 1 mL water was added. $BaBr_2$ solution was added into the ligand suspension. After stirring for 30 minutes, the liner was inserted into an autoclave and placed in an oven with the following temperature profile: heating from 20°C to 120°C during 2 hours, isothermal hold at 120°C for 48 hours, and cooling to 20°C during 12 hours. The synthesis resulted in colorless plate-shape single crystals.

*Synthesis of anhydrous MOF **II***: $Sr(OH)_2.8H_2O$ (78.66 mg, 0.296 mmol) was added into a mixture of H_6L (81 mg, 0.148 mmol), 4 mL DMF, 4 mL water, and 0.1 mL HCl (12M) in a 23 mL Teflon-liner Parr autoclave. After stirring for 30 minutes, the liner was inserted into an autoclave and placed in an oven with the following temperature profile: heating from 20°C to 120°C during 2 hours, isothermal hold at 120°C for 48 hours, and cooling to 20°C during 12 hours. The synthesis resulted in a polycrystalline product.

Analytical Techniques.

Powder X-ray Diffraction (PXRD): The samples were examined by PXRD for identification purposes and to assess phase purity Powder x-ray diffraction patterns were obtained by using a Rigaku Miniflex II bench top PXRD equipped with a Cu Kα X-ray source.

NMR Spectroscopy: ^1H, ^{13}C and ^{31}P NMR spectra were collected using a Bruker Advanced II 400 MHz NMR spectrometer.

Elemental Analyses: CHN analysis was performed using a Perkin Elmer Model 2400 series II. Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) was performed using a Philips XL30 ESEM equipped with a GSE detector with an accelerating voltage of 20 kV, and a 60 s acquisition time. Carbon and oxygen content from EDS data were excluded from the calculation of relative elemental composition ratios for accuracy.

ESI-MS Spectroscopy: data was collected using a methanol solution on a Bruker Esquire 3000.

Gas Adsorption Analysis: The adsorption isotherms for CO_2 (99.998%) and N_2 (99.999%) were conducted using an Accelerated Surface Area & Porosimetry System (ASAP) 2020 supplied by

Micromeritics Instruments Inc. The dry sample (~100 mg) was loaded into the glass analysis tube. The sample was heated under vacuum (~10^{-6} mbar) in two stages, initially to 60 °C at 1°C min^{-1} for 2 hrs then to 100°C at 1°C min^{-1} for 16 hrs. After this the outgas rate was less than 2 µbar hr^{-1}. The sample was then backfilled with N_2 before being transferred to the analysis port where it was evacuated for at least a further 120 min before the analysis was started.

Thermal Analysis: Thermal analysis (TG–DSC) data were recorded on a Netzsch STA 449C apparatus with a heating rate of 2 K /min using an aluminum pan as a reference standard under N_2 atmosphere.

Emission Measurements:

The fluorescence emission measurements were carried out using an Edinburgh Instruments FS5 Fluorescence Spectrometer. An SC-10 Front Face Sample Holder was used along with a solid-state cuvette. Solid-state quantum yield (QY) and lifetime measurements were also performed with the FS5, equipped with a standard xenon lamp (150W) and a standard PMT detector (R928P, Hamamatsu). EPL375 was used for excitation in lifetime measurements. Spectral and lifetime measurements were performed using SC-10 Front Face holder for Powders. QY measurements were performed using SC-30 Integrating Sphere module, and reported values based on triple independent measurements.

The humidity exposure was performed using a custom-made humidity chamber. Saturated salt solutions[2] were used to vary the humidity in the chamber. The chamber was equilibrated to the appropriate humidity for 24hrs prior to sample exposure. Samples were exposed to the respective humidities for an addition 24 hrs prior to analysis. All samples were excited at 408nm for comparative purposes.

The 0% humidity samples were prepared by drying in a vacuum oven at reduced pressure at 348K for 1 hour.

The 100% humidity samples were prepared by wetting the samples directly with deionised water until they changed colour from pale orange to pale fluorescent green.

The 29/30% humidity samples were prepared by enclosing the sample in a humidity chamber with a saturated LiCl solution for 24 hours.

The 50/51% humidity samples were prepared by enclosing the sample in a humidity chamber with a saturated solution of K_2CO_3 for 24 hours.

The 61/64% humidity samples were prepared by enclosing the sample in a humidity chamber with a saturated solution of NaCl for 24 hours.

The 84/85% Humidity samples were prepared by enclosing the sample in a humidity chamber with a beaker containing deionised water for 24 hours.

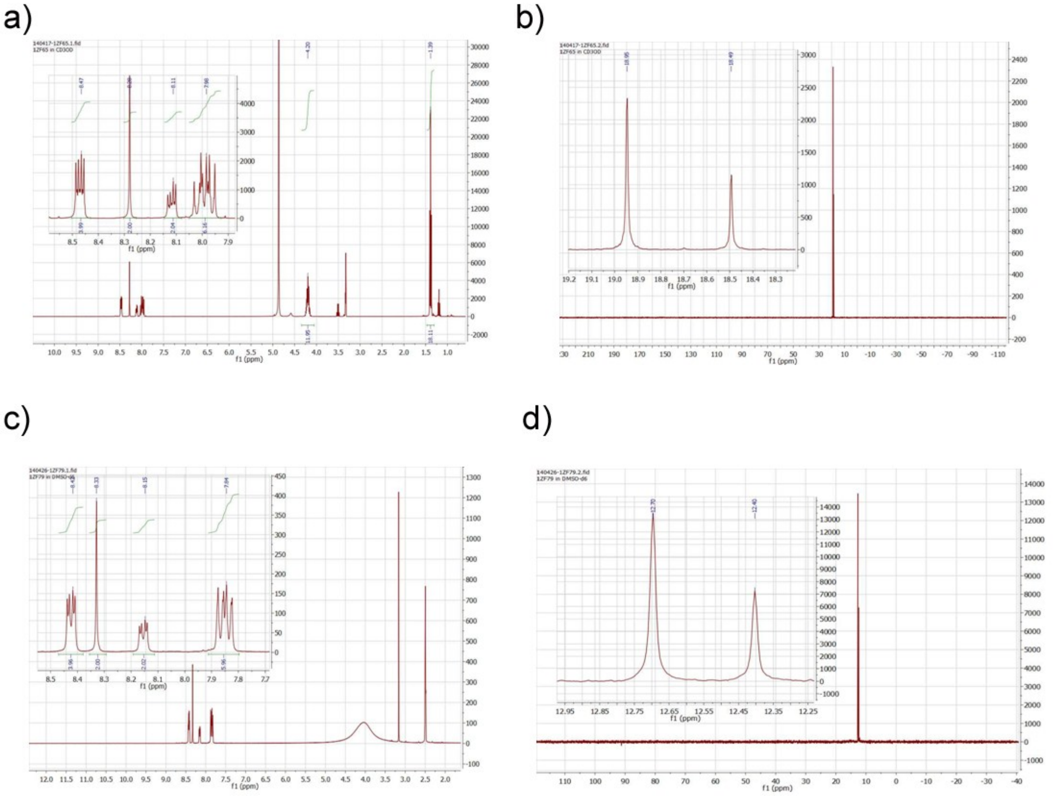
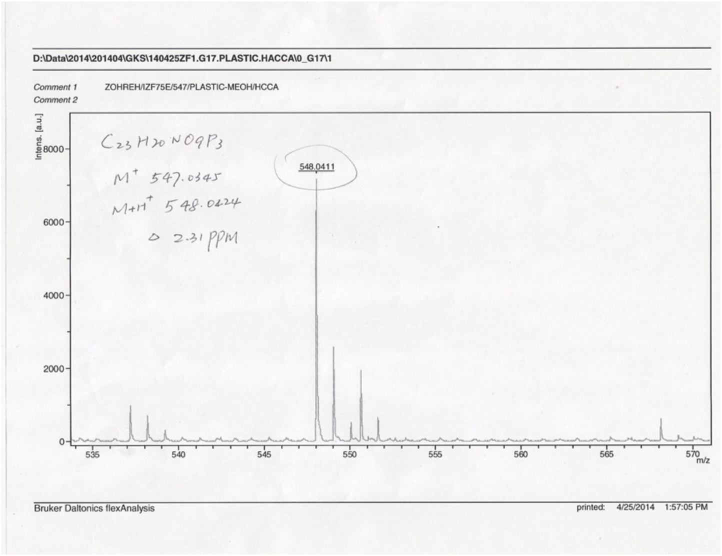


Figure S1. Proton spectrum



D:\Data\2014\201404\GKS\140425ZF1.G17.PLASTIC.HACCA\0_G17\1

Comment 1 ZOHREH/IZF75E/547/PLASTIC-MEOH/HCCA

Comment 2

$C_{23}H_{20}NO_9P_3$

M^+ 547.0345

$M+H^+$ 548.0424

Δ 2.31 PPM

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Figure S2.

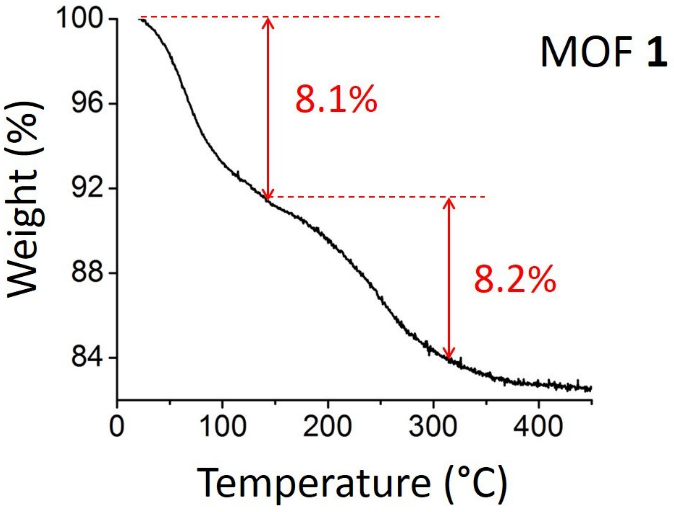


Figure S3. TGA analysis of MOF **1**.

EA: calc., C: 32.42, H: 3.24, N: 2.91; **Actual**, C: 32.44, H: 2.93, N: 2.67

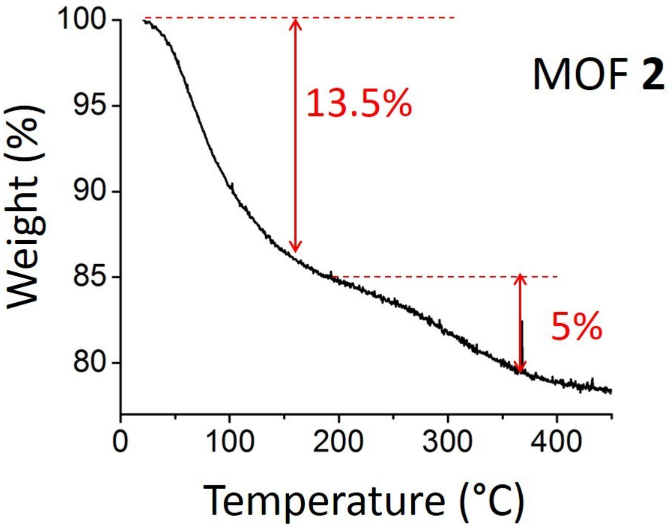


Figure S4. TGA analysis of MOF **2**.

EA: calc., C: 34.45, H: 3.60, N: 2.46; **Actual**, C: 32.46, H: 3.08, N: 1.72

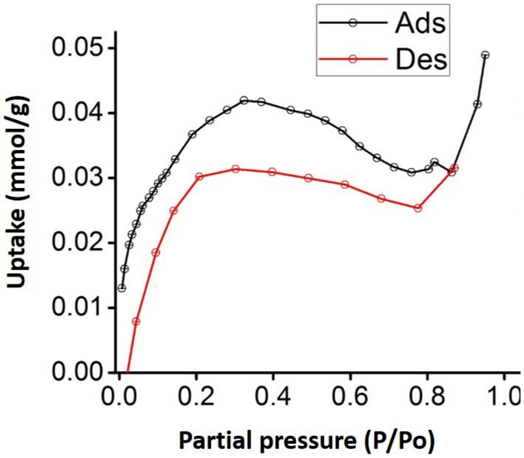


Figure S5. N_2 isotherm at 77 K for MOF **1** showing essentially a non-porous structure.

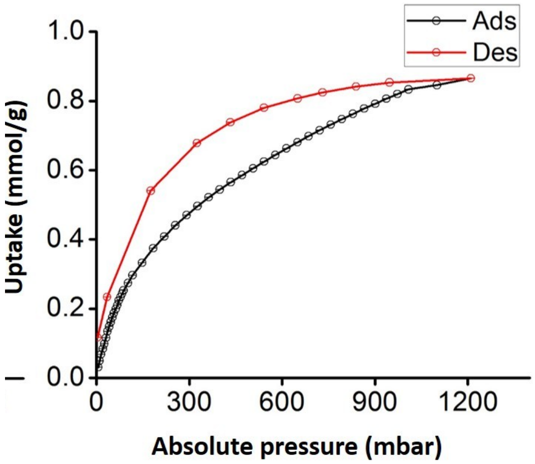
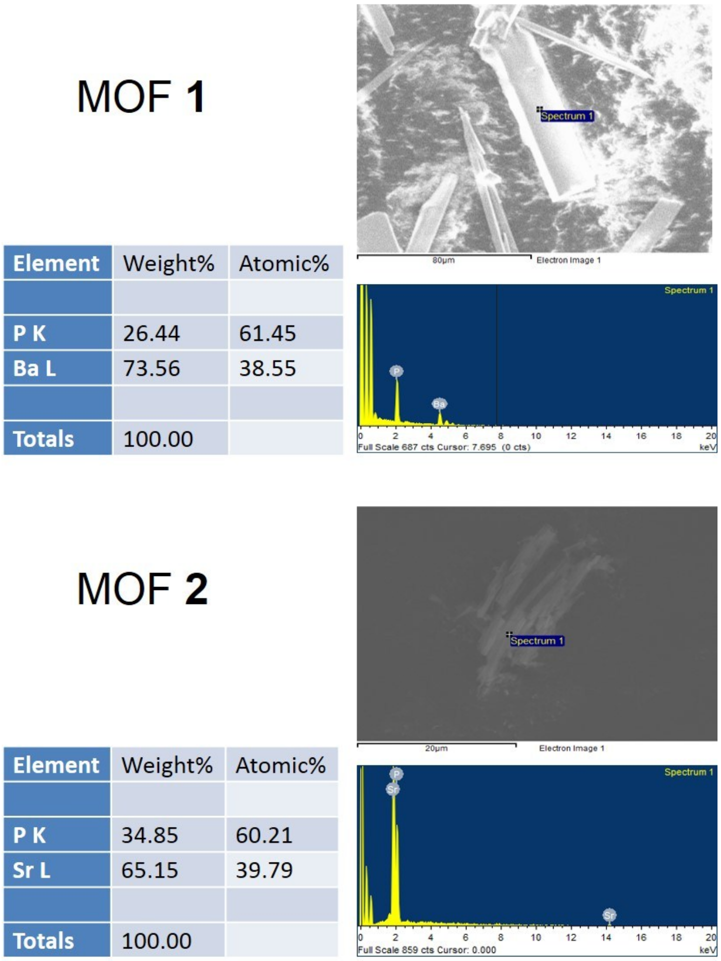


Figure S6. CO_2 isotherm at 273 K for MOF **1** showing slightly higher uptake than N2 owing to the smaller kinetic diameter of CO_2 and the facilitated micropore diffusion at 273K versus 77K.



MOF **1**

Element	Weight%	Atomic%
P K	26.44	61.45
Ba L	73.56	38.55
Totals	100.00	

MOF **2**

Element	Weight%	Atomic%
P K	34.85	60.21
Sr L	65.15	39.79
Totals	100.00	

Figure S7. SEM images and EDX analyses of the MOF **1** and MOF **2**.

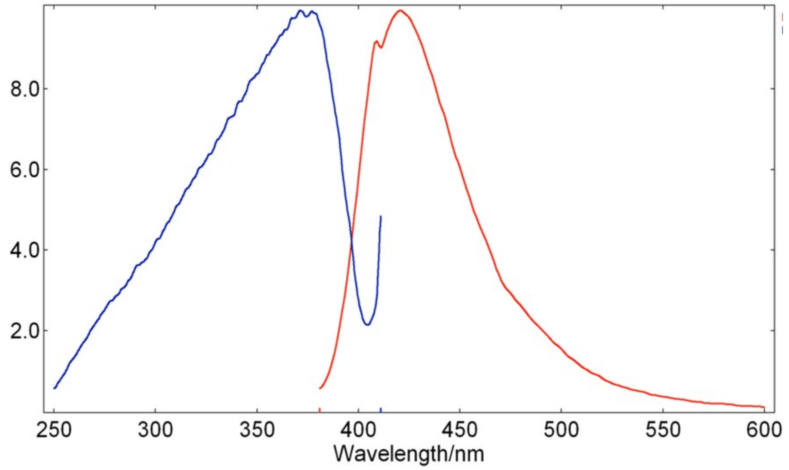


Figure S8. Normalized excitation (blue) and emission (red) spectra of powdered *dry* H_6L (λ_{ex} = 371 nm, λ_{em} = 421 nm).

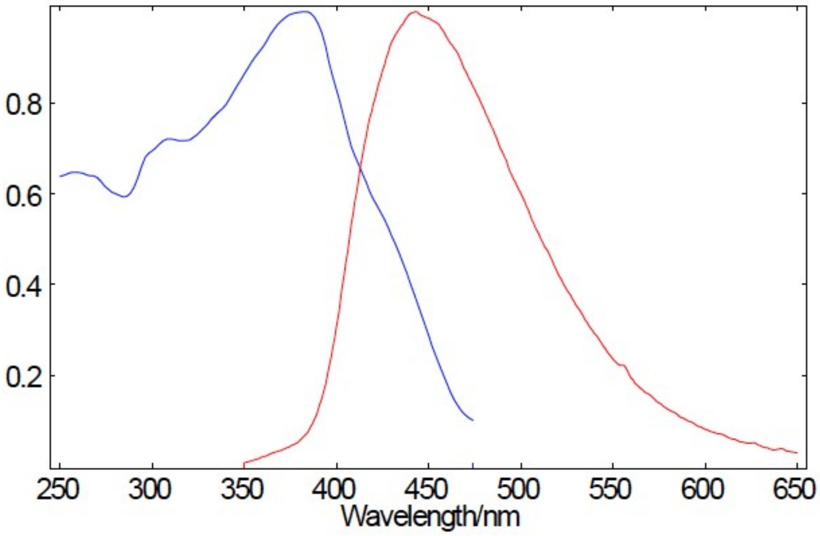


Figure S9. Normalized excitation (blue) and emission (red) spectra of powdered *dry* (prior to treatment with H_2O) MOF-1 (Ba) (λ_{ex} = 330 nm, λ_{em} = 500 nm).

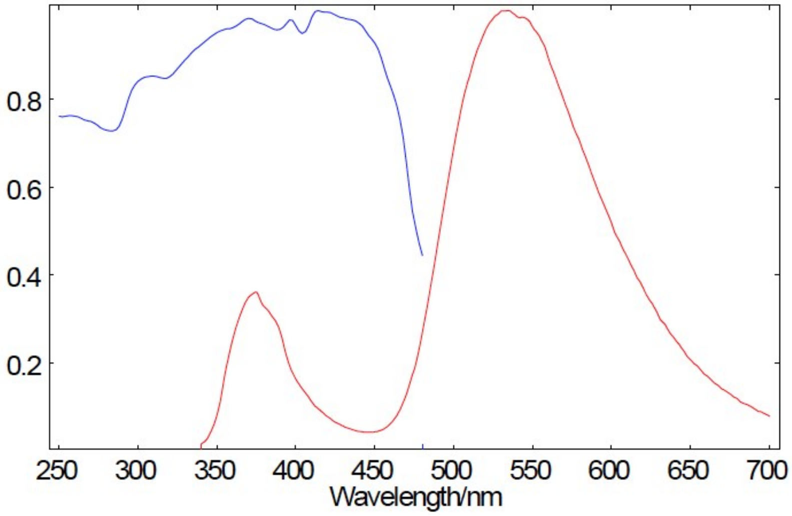


Figure S10. Normalized excitation (blue) and emission (red) spectra of powdered *wet* (with H_2O) MOF-1 (Ba) (λ_{ex} = 330 nm, λ_{em} = 500 nm).

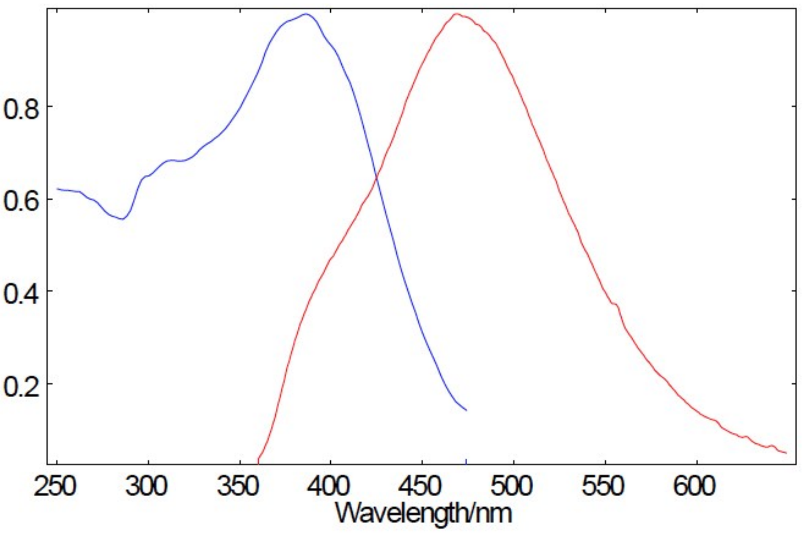


Figure S11. Normalized excitation (blue) and emission (red) spectra of powdered *re-dried* (H_2O removed by evaporation; result confirmed by both air dry and by Vacuum Oven) MOF-1 (Ba) (λ_{ex} = 330 nm, λ_{em} = 500 nm).

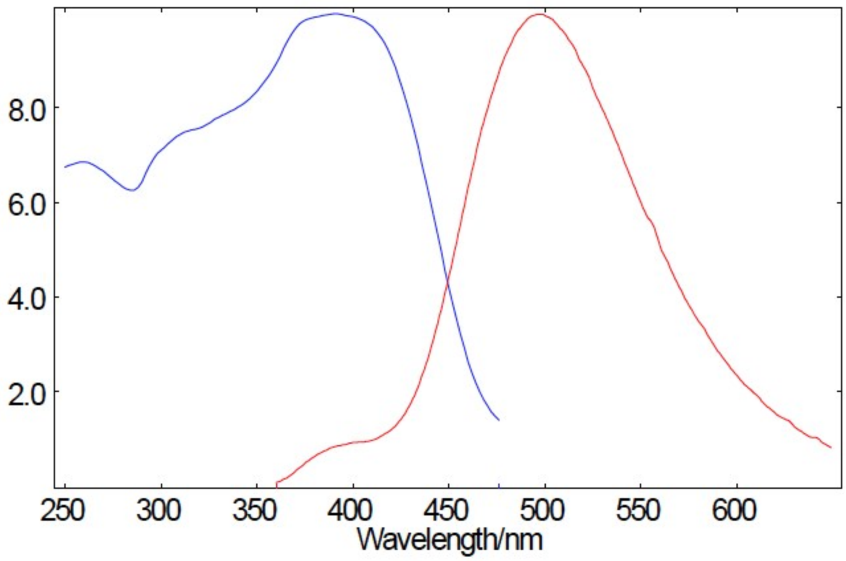


Figure S12. Normalized excitation (blue) and emission (red) spectra of powdered *dry* (prior to treatment with H_2O) MOF-2 (Sr) (λ_{ex} = 330 nm, λ_{em} = 500 nm).

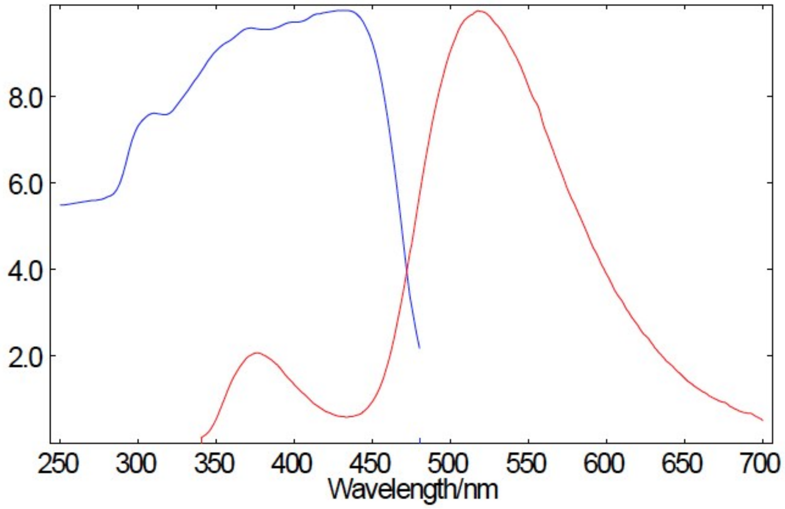


Figure S13. Normalized excitation (blue) and emission (red) spectra of powdered *wet* (with H_2O) MOF-2 (Sr) (λ_{ex} = 330 nm, λ_{em} = 500 nm).

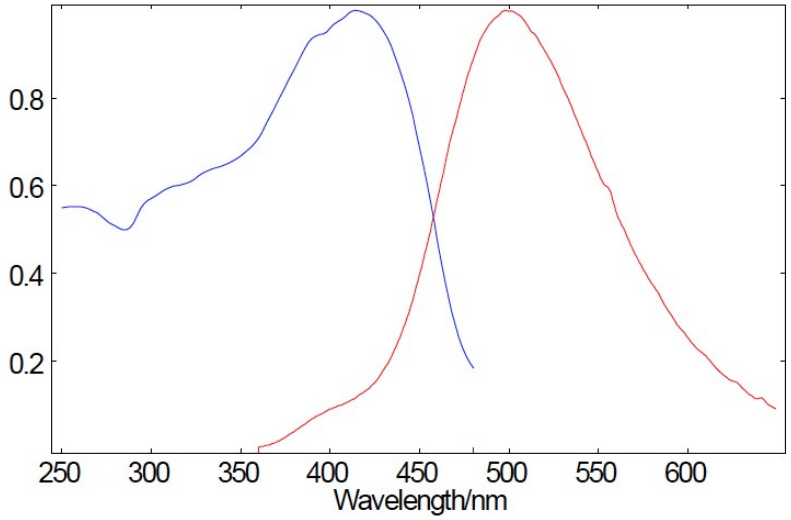


Figure S14. Normalized excitation (blue) and emission (red) spectra of powdered *re-dried* (H_2O removed by evaporation; result confirmed by both air dry and by Vacuum Oven) MOF-2 (Sr) (λ_{ex} = 330 nm, λ_{em} = 500 nm).

Table S1. Solid-state QY measurements of both MOF-1 (Ba) and MOF-2 (Sr) in representative states of hydration (λ_{ex} = 330 nm). As noted above, reported values are based on triple independent measurements with all values showing less than 0.7% variance.

	MOF-1 (Ba)			MOF-2 (Sr)			Ligand
	Dry	Wet	Redried	Dry	Wet	Redried	
QY%	9.9	16.1	7.1	8.7	14.3	6.4	7.2

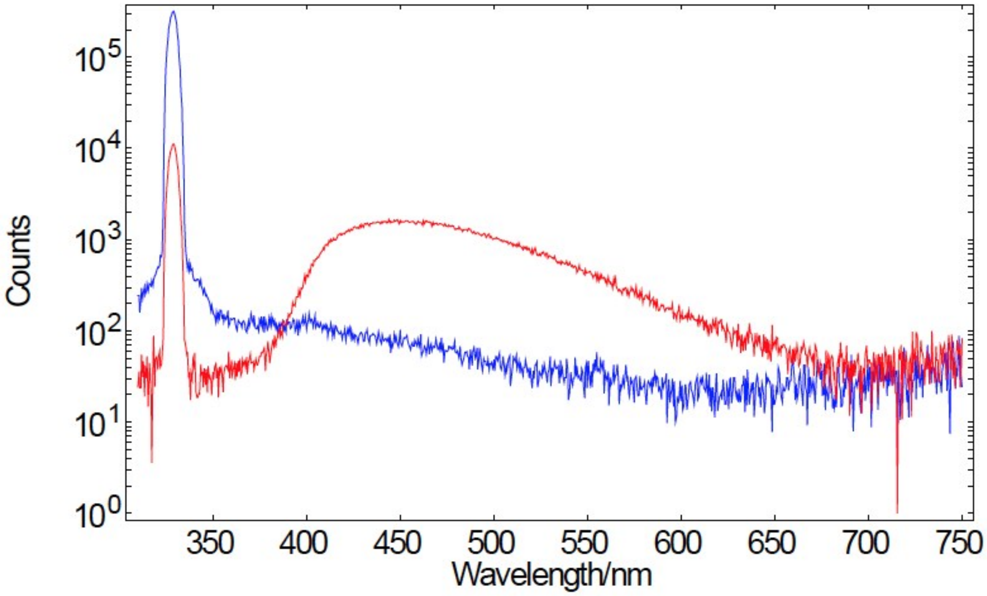


Figure S15. Example measurement of QY evaluation for the initially dry MOF-1 (Ba).

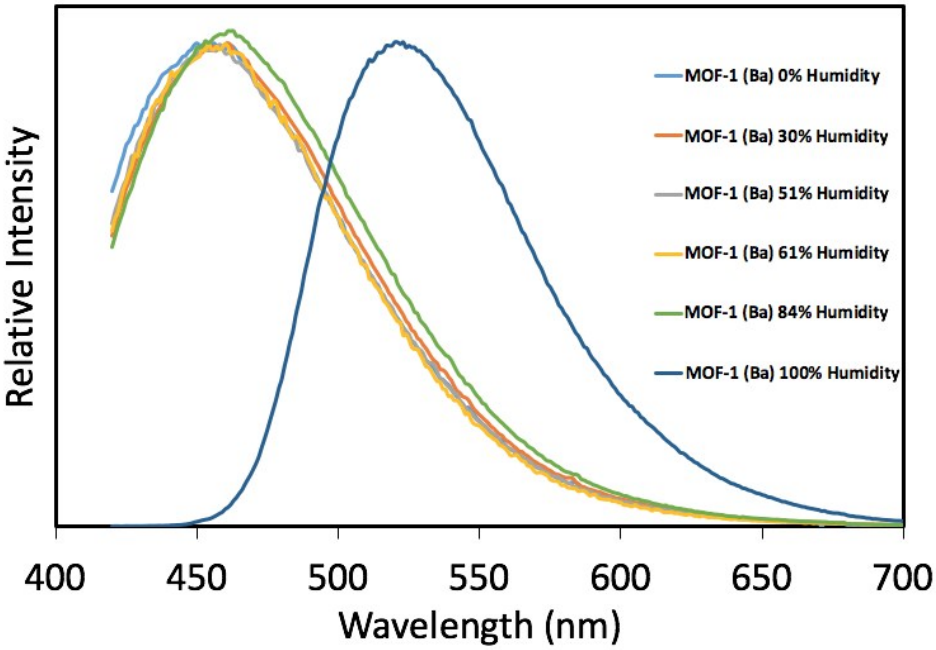


Figure S16. Normalized emission of powdered MOF-1 (Ba) exposed to varying degrees of humidity showing a sharp red shift in $\boldsymbol{\lambda}_{\mathbf{max}}$ during complete hydration (λ_{ex} = 408 nm).

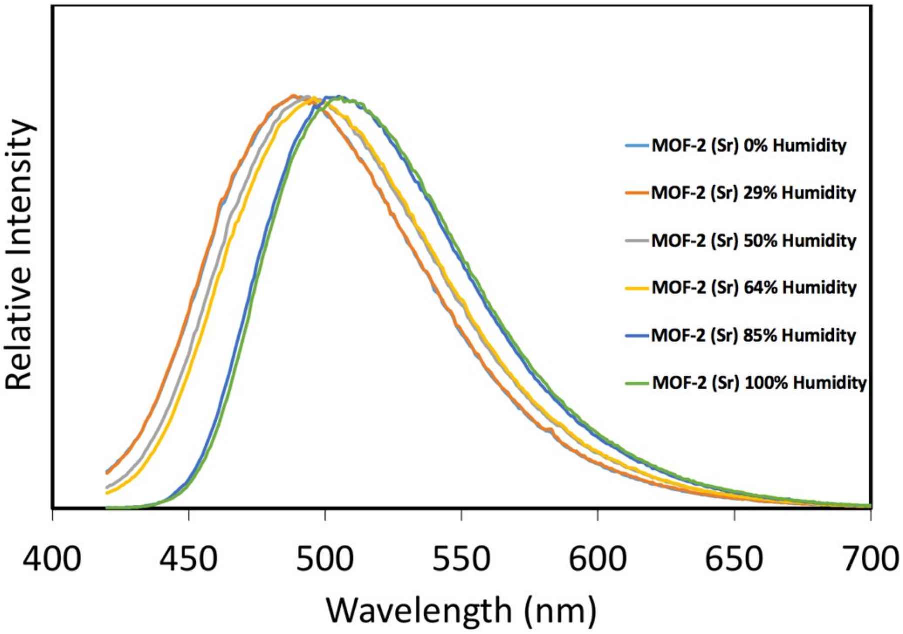


Figure S17. Normalized emission of powdered MOF-2 (Sr) exposed to varying degrees of humidity showing a gradual red shift in $\boldsymbol{\lambda}_{\mathbf{max}}$ with increasing humidity (λ_{ex} = 408 nm).

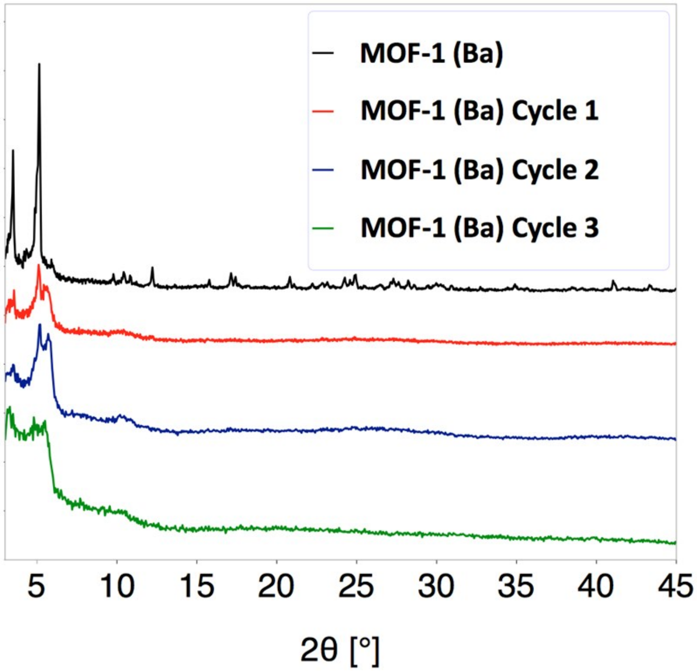


Figure S18. PXRD pattern overlay of MOF-1 (Ba)after subsequent Wet/Dry cycles showing a decrease in crystallinity after each hydration.

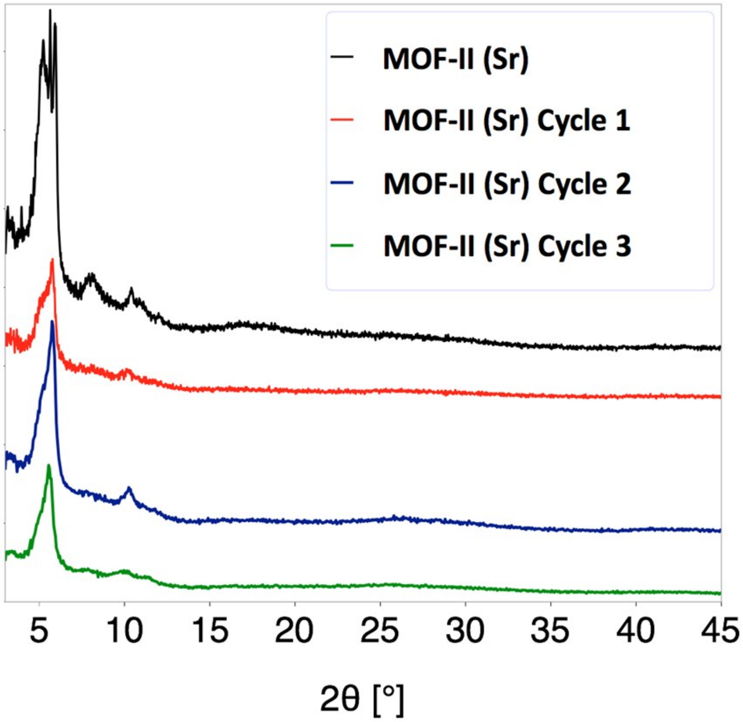


Figure S19. PXRD pattern overlay of MOF-2 (Sr)after subsequent Wet/Dry cycles showing a decrease in crystallinity after each hydration.

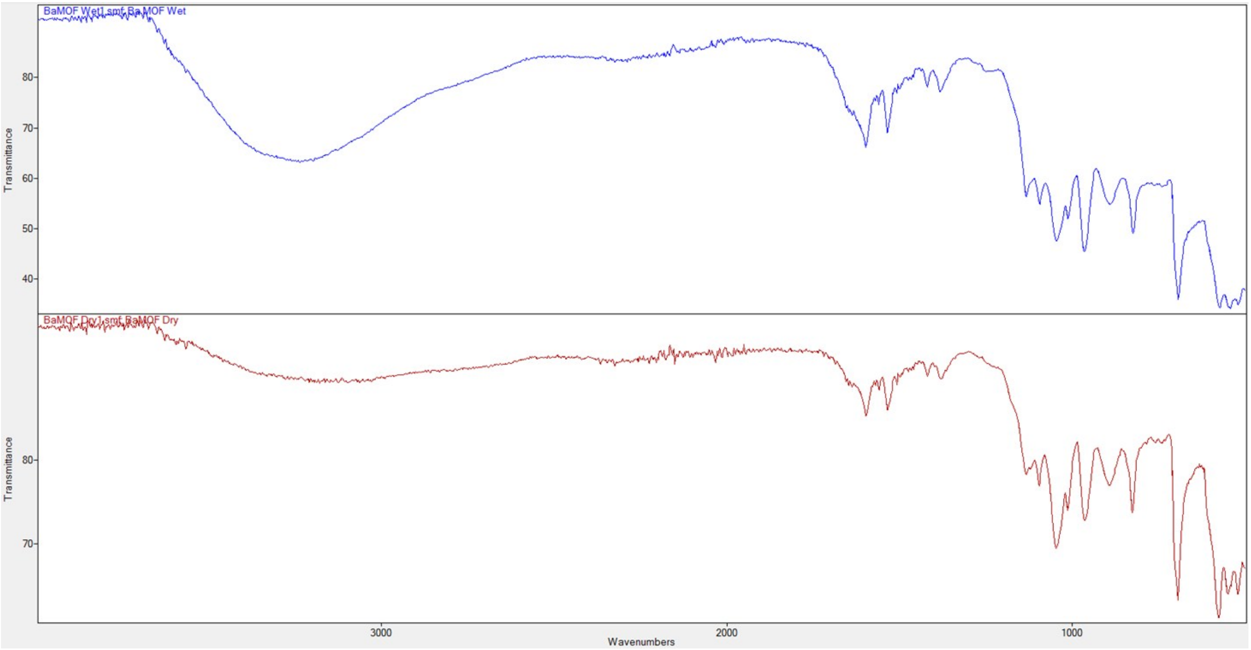


Figure S20. IR transmittance spectrum of MOF-1 (Ba) Dry (Red) and Wet (Blue) collected on a Shimadzu IR Affinity-1 spectrometer (diamond cell).

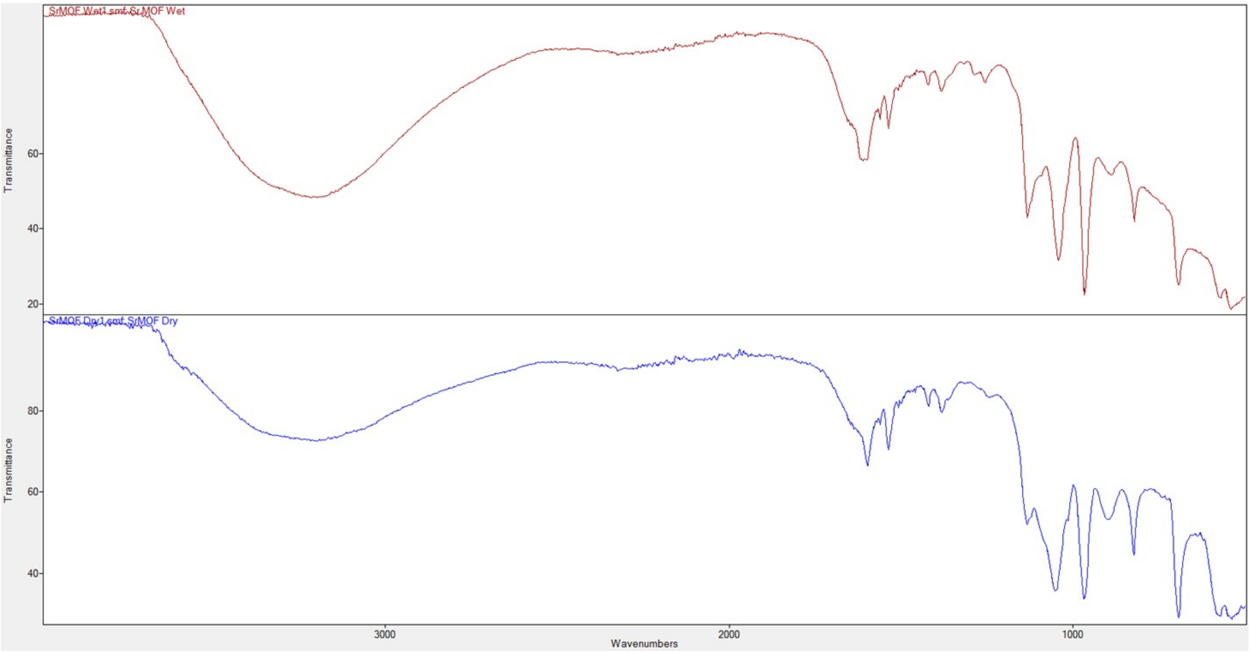


Figure S21. IR transmittance spectrum of MOF-2 (Sr) Dry (Red) and Wet (Blue) collected on a Shimadzu IR Affinity-1 spectrometer (diamond cell).

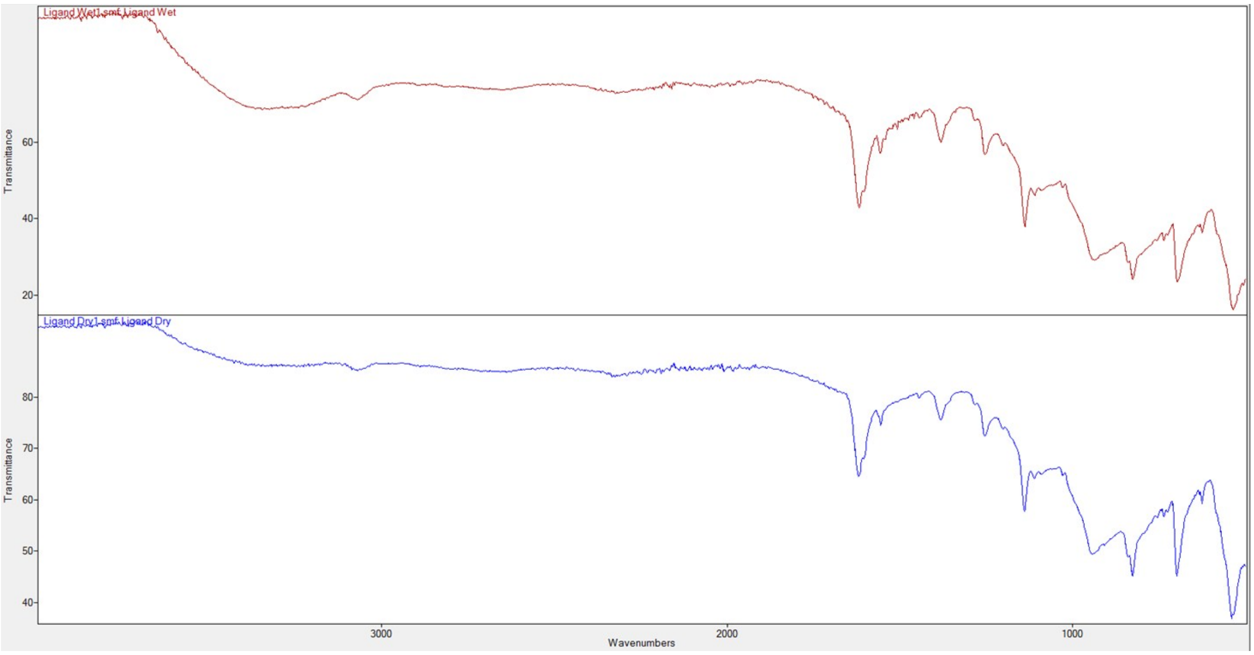


Figure S22. IR transmittance spectrum of H_6L Dry (Red) and Wet (Blue) collected on a Shimadzu IR Affinity-1 spectrometer (diamond cell).

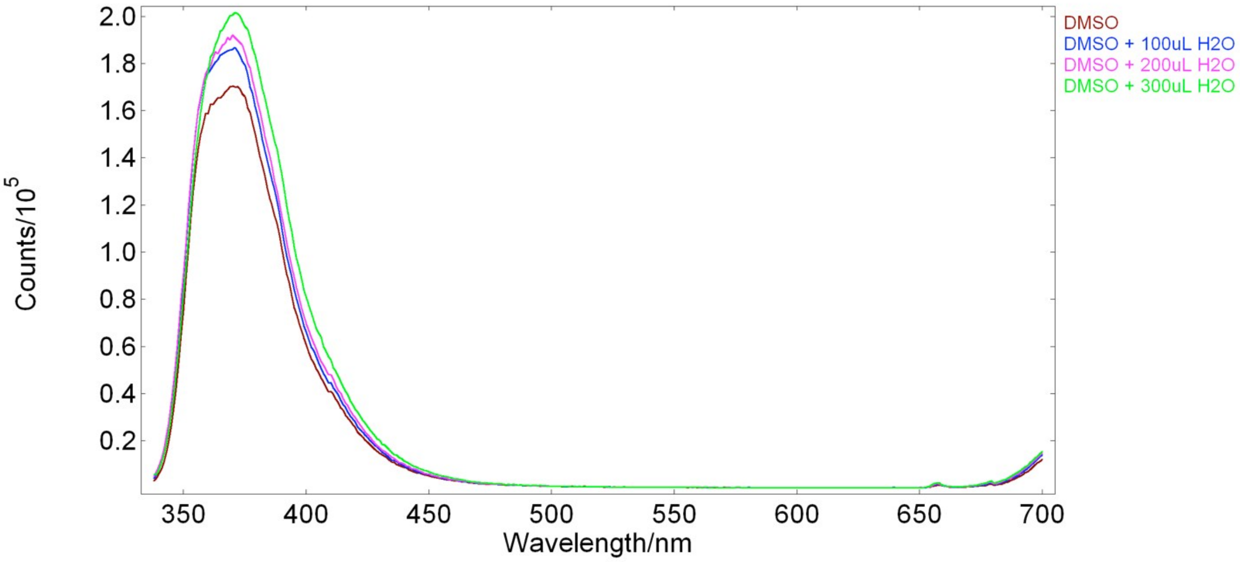


Figure S23. Overlay of emission spectra obtained of H_6L in DMSO with 3 subsequent additions of H_2O (λ_{ex} = 328 nm; H_6L at $1x10^{-5}$M, 298 K).

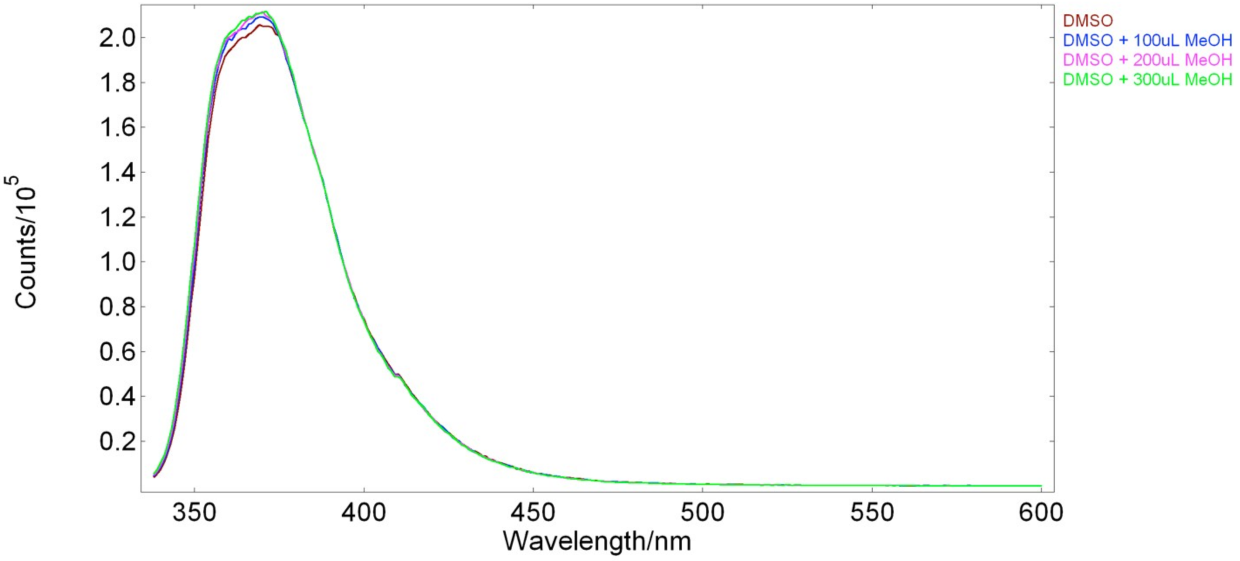


Figure S24. Overlay of emission spectra obtained of H_6L in DMSO with 3 subsequent additions of MeOH (λ_{ex} = 328 nm; H_6L at $1x10^{-5}$M; 298 K).

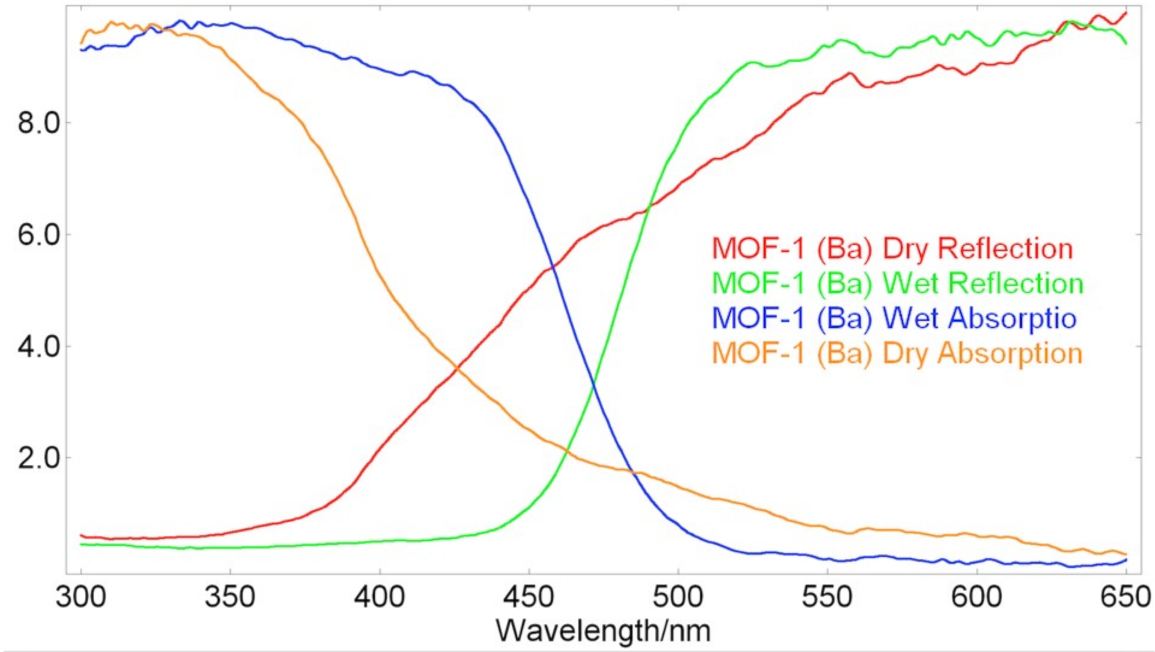


Figure S25. Normalised Reflection and Absorption data for Wet and Dry powdered MOF-1 (Ba).

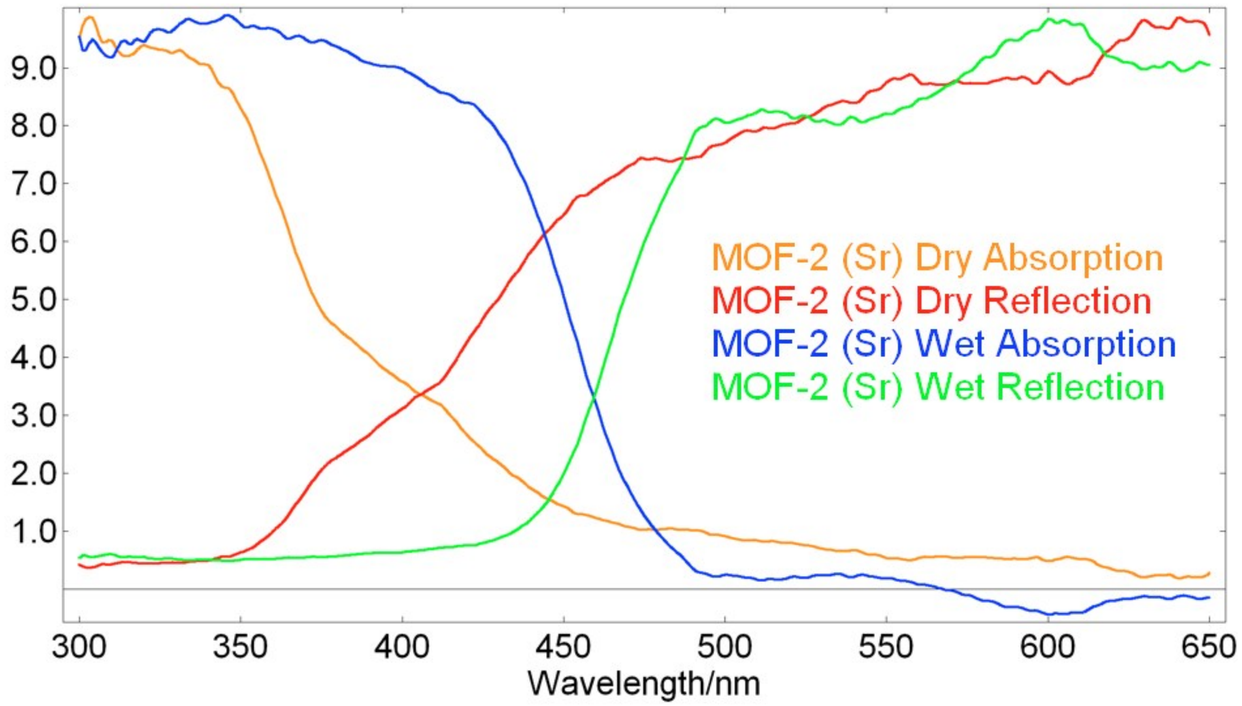


Figure S26. Normalised Reflection and Absorption data for Wet and Dry powdered MOF-2 (Sr).

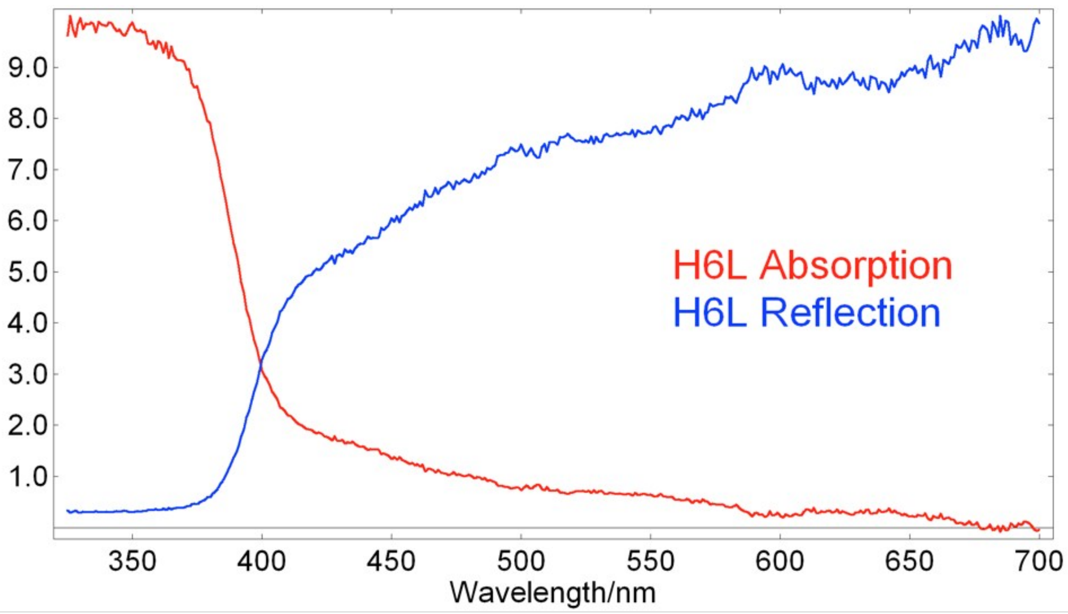


Figure S27. Normalised Reflection and Absorption data for Dry powdered H_6L.

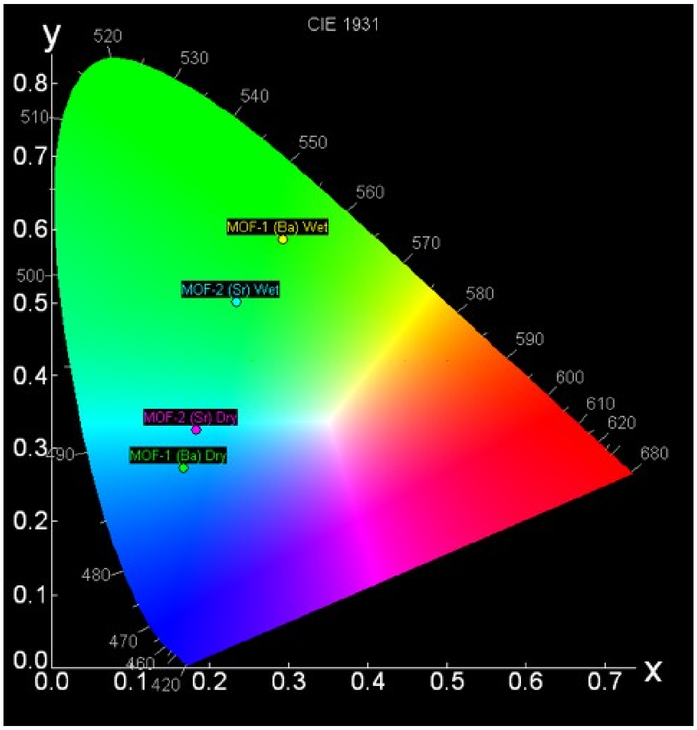


Figure S28. Chromaticity diagram illustrating CIE of MOFs **1** and **2** in both hydrated and dehydrated states.

Crystal Structure Determination.

Single crystal X-ray diffraction data was collected at the Canadian Macromolecular Crystallography Facility CMCF-BM beamline at the Canadian Light Source.[3] CMCF-BM is a bending magnet beamline with a Si (111) double crystal monochromator, Rayonix MX300HE CCD detector and MD2 microdiffractometer equipped with Mini Kappa Goniometer Head.

Data was collected at 18.000 KeV (0.68881 Å). All data was collected at low temperature (100 K). Cell refinement and data reduction were performed using Mosflm. [4] An empirical absorption correction, based on the multiple measurements of equivalent reflections, and merging of data was performed using SADABS.[5] Data conversion from XDS file format to SADABS file format was performed using XDS2SAD.[6] The space group was confirmed by XPREP[7] routine.

The structures were solved by direct-methods and refined by full-matrix least squares and difference Fourier techniques with SHELXL-2014.[8]

All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were set in calculated positions and refined as riding atoms with a common thermal parameter. Disorders of aromatic rings were modeled as two-component disorders using PART instructions and atom occupancy were refined using free variables.

Table S2. Crystallographic and refinement details of MOF **1** at 100 K.

	1
chemical formula	C46H29.41Ba3.99N2O20P6
crystal colour	Colourless
***Fw*; *F*(000)**	1664.28; 6344
***T* (K)**	100(2)
wavelength (Å)	0.688790
space group	C2/c
***a* (Å)**	43.611(9)
***b* (Å)**	8.5490(17)
***c* (Å)**	34.589(3)
α (deg)	90
β (deg)	103.59(3)
γ (deg)	90
Z	8
***V* (Å^3)**	12535(4)
ρ_{calcd} (g·cm^{-3})	1.764
μ (mm^{-1})	2.695
θ range (deg); completeness	1.661 – 25.000; 0.996
collected reflections; R_σ	44495; 0.0508
unique reflections; R_{int}	44495; 0.0537
R1[a]; wR2[b] [I > 2σ(I)]	0.0873; 0.2307
R1; wR2 [all data]	0.0976; 0.2370
GOF	1.053
largest diff peak and hole	2.127 and -1.146

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

References:

[1] Mikroyannidis, J. A.; Ye, S.; Liu, Y. Synthetic Metals **2009**, *159*, 492. [2] Rockland, L. B. *Analytical Chemistry* **1960**, *32*, 1375. [3] Grochulski, P.; Fodje, M. N.; Gorin, J.; Labiuk, S. L.; Berg, R. J Synchrotron Rad, J Synchrotron Radiat **2011**, *18*, 681–684. [4] Kabsch, W. Automatic processing of rotation diffraction data from crystals of initially unknown symmetry and cell constants. *J. Appl. Cryst*. **1993**, *26*, 795-800. [5] T.G.G. Battye, L. Kontogiannis, O. Johnson, H.R. Powell and A.G.W. Leslie *Acta Cryst*. **2011**, *D67*, 271-281.
[6] Sheldrick, G. M. Sadabs; University of Göttingen, Germany Program for Empirical Absorption Correction of Area Detector Data, **1996**. [7] Sheldrick, G. M. **2008** XDS2SAD. University of Gottingen, Germany. [8] XPREP **2014**; X-ray data Preparation and Reciprocal space Exploration Program.Bruker AXS Inc., Madison, Wisconsin, USA.