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Supplementary Information for

Luminescent Cationic Metal–Organic Framework Featuring [Cu–Pyrazolate]$_3$ Units for Volatile Organic Compound Sensing

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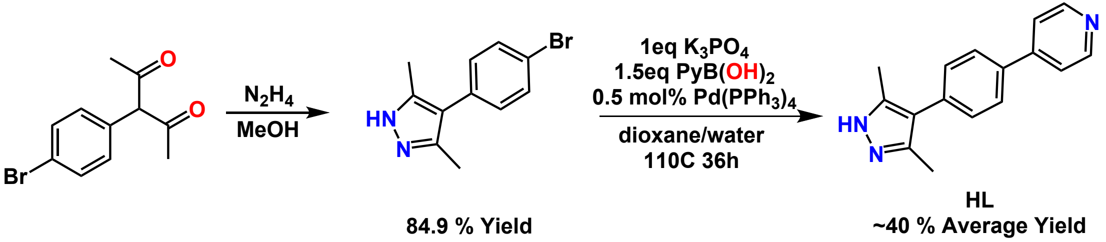
General Considerations:

Elemental analyses were performed at the ALANEST Facility in our Chemistry Department on a on a Thermo Flash 2000 CHN analyzer. Thermogravimetric analyses (TGA) were performed on a TA Instruments SDT Q600 instrument under a dinitrogen atmosphere with a heating rate of 5 °C per minute. NMR spectra were recorded on a Bruker Avance 400 spectrometer. Both ^{1}H and ^{13}C NMR spectra were referenced and reported relative to the solvent's residual signals. Photoluminescence spectra were measured using a QunataMaster spectrofluorimeter (Photon Technology International, Edison, New Jersey) with a Xenon lamp for steady-state measurements. Steady-state photoluminescence spectra for quantum yield measurements were recorded on a Horiba Fluorolog-3 spectrofluorimeter equipped with a Xenon lamp excitation source and a Quanta-Phi quantum yield measurement accessory. Photoluminescence lifetimes were measured using a Horiba Time-Correlated Single Photon Counting setup with a 375 nm picosecond laser (DeltaDiode Horiba). Sample emission was detected at 575 nm after passing through a spectrometer (iHR320, Horiba) and detected on a single photon detector (PPD, Horiba). Powder X-Ray Diffraction (PXRD) experiments were performed on a Rigaku MiniFlex 600 diffractometer equipped with a Cu-Kα source operating at 40 kV/15 mA at the Walter Curlook Materials Characterization & Processing Laboratory at the University of Toronto Department of Materials Science and Engineering. A step scan mode was used for data acquisition with a step size of 0.02° 2θ. All the PXRD samples were prepared by dropcasting onto a silicon zero background sample holder. The infrared spectrum of **1** was recorded using a neat sample on a Bruker Alpha FT-IR spectrometer equipped with a Platinum ATR sampling unit in air. Unless otherwise stated, all manipulations were performed under dinitrogen and all reagents were purchased from commercial sources and used without further purification. DMF for the self-assembly of MOFs was dried and degassed on a PureSolv-MD (Innovative Technology, Inc., Newburyport, Maryland) Solvent Purification System containing activated alumina. 4-(4-bromophenyl)-2,4-pentadione was prepared following literature procedures.[1] $Pd(PPh_3)_4$ was synthesized following modified standard procedures from $Pd(OAc)_2$.[2]

Compound Synthesis:



Scheme S1. Synthesis of **HL** ligand

<u>Synthesis of 4-(4-bromophenyl)-3,5-dimethyl-1H-pyrazole (Done in air):</u>

To a suspension of 3-(4-bromophenyl)pentane-2,4-dione (25.0 g, 980 mmol) in methanol (350 mL) was added 12 N HCl aq. (1 mL). The resulting mixture was then cooled in an ice bath and hydrazine monohydrate was added dropwise (11.9 mL, 245 mmol). The reaction mixture was further stirred for 1 h at 0°C before being left to react overnight at room temperature. The solution was concentrated under reduced pressure until the volume was halved and the remaining solution was cooled in a –20°C freezer. White crystals of **1** were collected via vacuum filtration, washed with cold methanol, and dried under vacuum (20.9 g, 84.9 % yield). A second and third crop of crystals may be collected from the supernatant. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 11.61 (s, N-H), 7.53 (d, J = 8.4 Hz, 2H, Ph), 7.14 (d, J = 8.4 Hz, 2H, Ph), 2.32 (s, 6H, Me). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.90, 132.82, 131.72, 131.00, 120.35, 117.52, 11.64. Anal. Cacld. for $C_{11}H_{10}N_2Br$: C 52.61, H 4.42, N 11.16; found C 52.68, H 4.74, N 11.38.

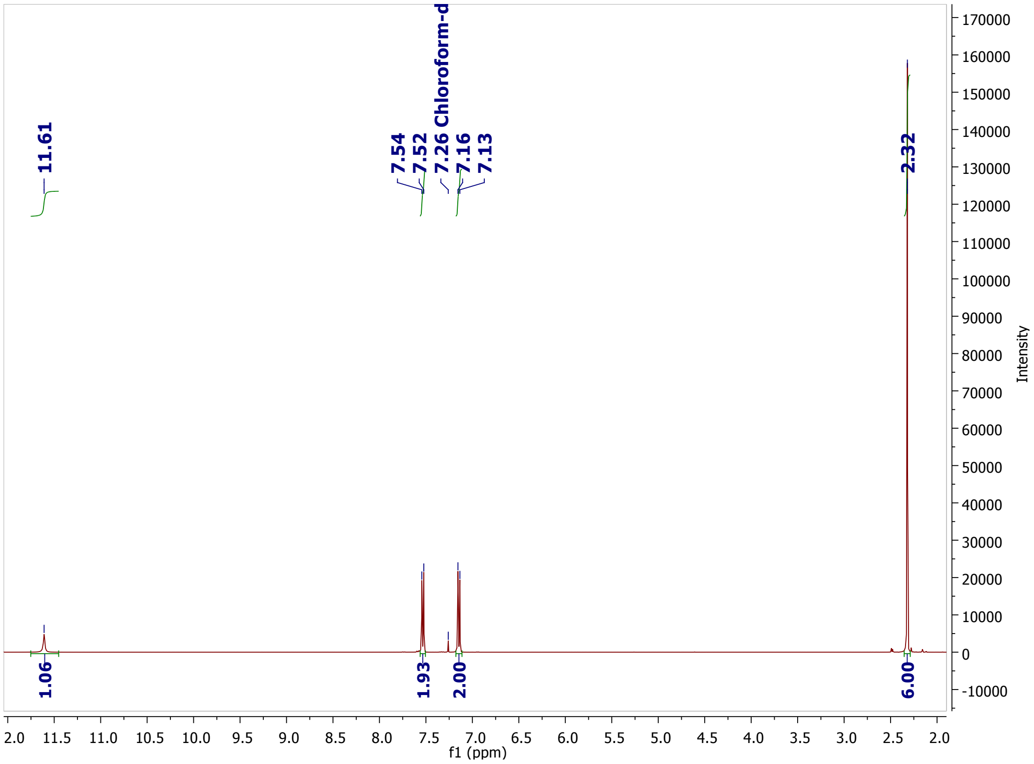


Figure S1. ^{1}H NMR in $CDCl_3$ of 4-(4-bromophenyl)-3,5-dimethyl-1H-pyrazole

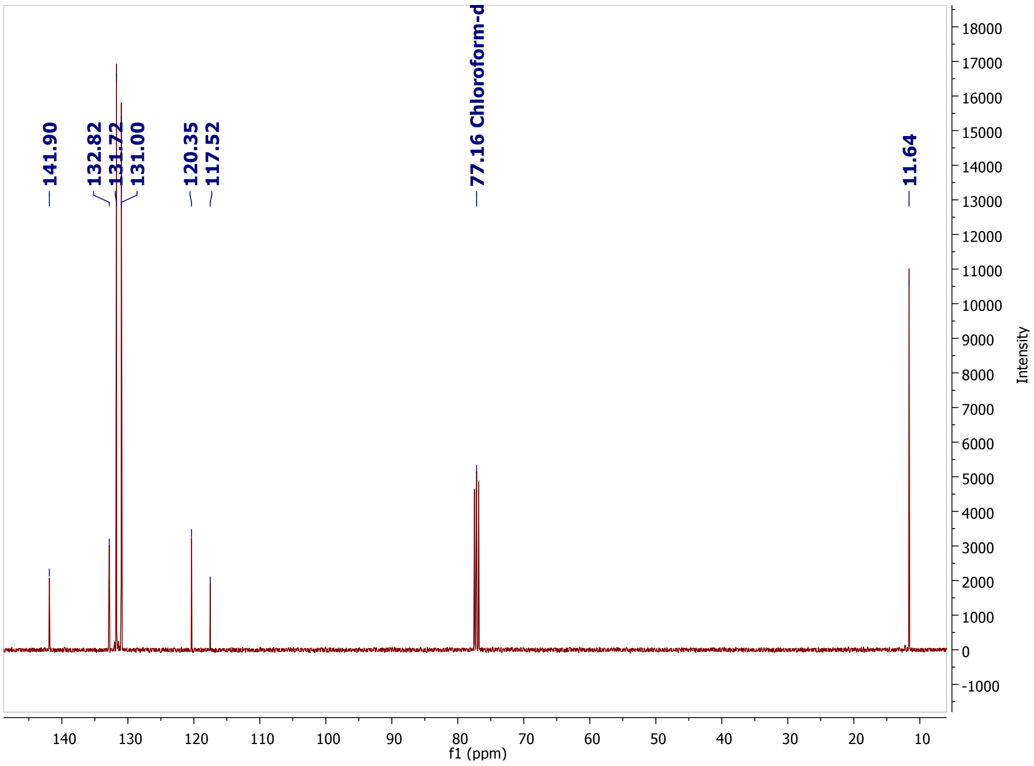


Figure S2. ^{13}C NMR in $CDCl_3$ of 4-(4-bromophenyl)-3,5-dimethyl-1H-pyrazole

Synthesis of 4-(4-(3,5-dimethyl-1H-pyrazol-4-yl)phenyl)pyridine, **HL**:

To a degassed mixture of 4-(4-bromophenyl)-3,5-dimethyl-1H-pyrazole **(**7.50 g, 29.9 mmol), K_3PO_4 (6.34 g, 29.9 mmol), 4-pyridine boronic acid (4.22 g, 34.3 mmol), and $Pd(PPh_3)_4$ (172.6 mg, 0.149 mmol) was added 360 mL of degassed dioxane/water (1:1) mixed solvent. The resulting reaction mixture was then refluxed and the reaction progress was monitored via TLC. Upon completion (2–3 days) the solution was made alkaline with 4 g of KOH in 150 mL of water and extracted with ethyl acetate (4 x 100 mL). The organic extracts were combined, washed with brine, dried over $MgSO_4$, filtered, and concentrated to dryness under reduced pressure to yield 7 g of crude material which was purified via column chromatography (eluent begins as EtOAc and switches to 5% MeOH in EtOAc) to produce 5.02 g (67.4 % yield) of the pure product. Note that **HL** reacts with chloroform. ^1H NMR (400 MHz, DMSO-d_6) δ 12.38 (s, 1H, NH), 8.63 (d, J = 6.1 Hz, 2H, Py), 7.85 (d, J = 8.4 Hz, 2H, Ph), 7.74 (d, J = 6.1 Hz, 2H, Py), 7.45 (d, J = 8.4 Hz, 2H, Ph), 2.24 (s, 6H, Pz-Me). ^{13}C NMR (100 MHz, DMSO-d_6) δ 150.21, 146.69, 145.13. 136.08 135.24, 134.20, 129.27, 126.84, 120.94, 116,14, 12.99, 10.16. Anal. Cacld. for $C_{16}H_{15}N_3$: C 77.08, H 6.06, N 16.85; found C 77.13, H 5.89, N 16.64.

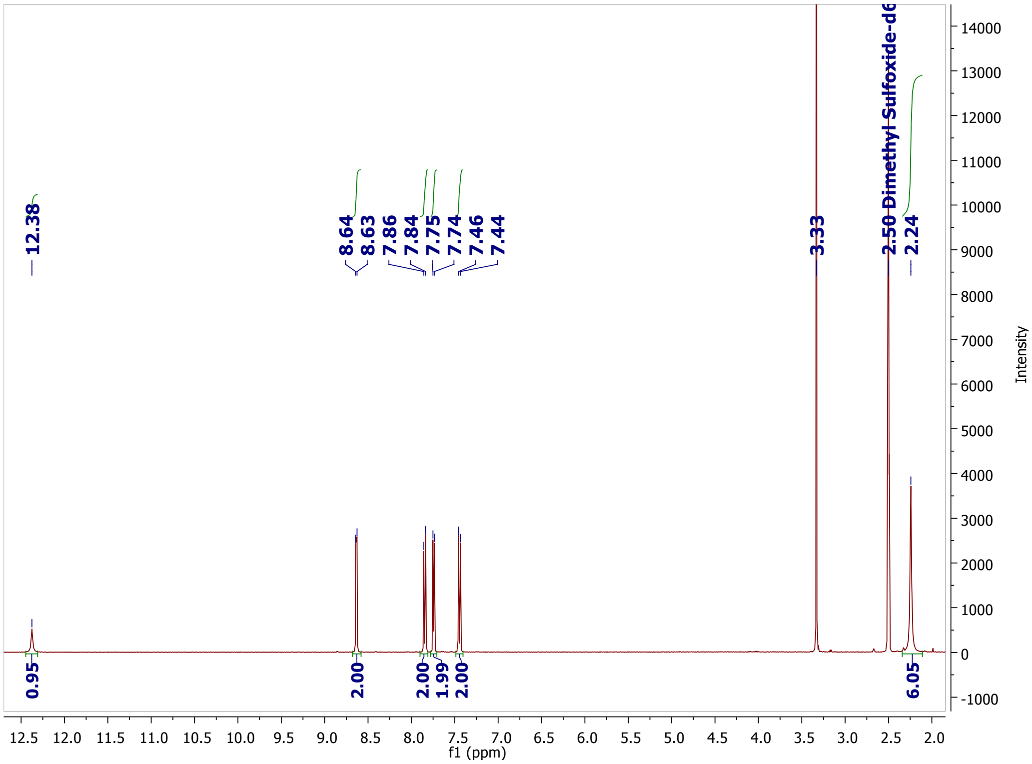


Figure S3. ^1H NMR of **HL** in DMSO-*d_6*

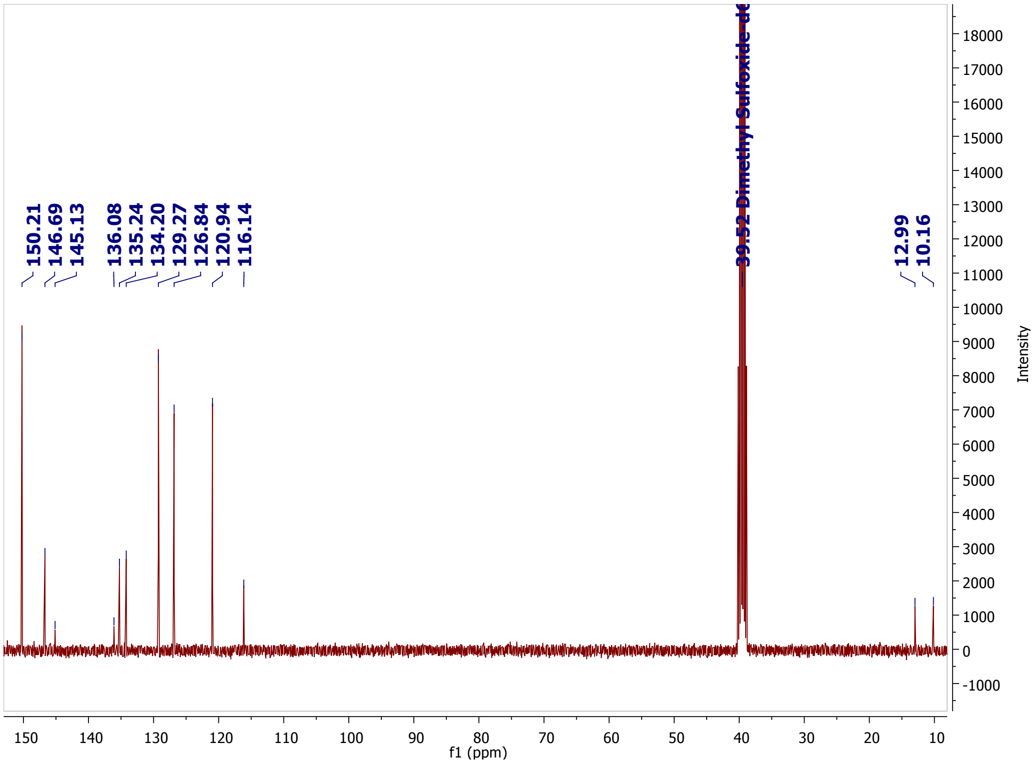


Figure S4. ^{13}C NMR of **HL** in DMSO-d_6

Synthesis of MOF **1**:

Approximately 100 mL of DMF was transferred to a dry, degassed mixture of **HL** (182.3 mg, 0.7312 mmol) and CuBr (129.3 mg, 0.9014 mmol) in a 350 mL Schlenk bomb. The orange mixture was subjected to three consecutive freeze-pump-thaw cycles and backfilled with nitrogen. The Schlenk bomb was sealed, covered with aluminum foil, and heated with gentle stirring at 135°C for 5 d. The resulting yellow crystals were collected via vacuum filtration and washed with acetone and hexanes, dried under vacuum, and stored under N_2. 115.9 mg (52.6 % yield) of yellow micro-crystals collected. X-ray quality crystals may be collected by not stirring the reaction mixture at the cost of reduced yield. Anal. Cacld. for vacuum dried $C_{48}H_{42}N_9Br_2Cu_5$: C 47.16, H 3.46, N 10.31; found C 46.54, H 2.93, N 10.20.

Further structural description of MOF 1:

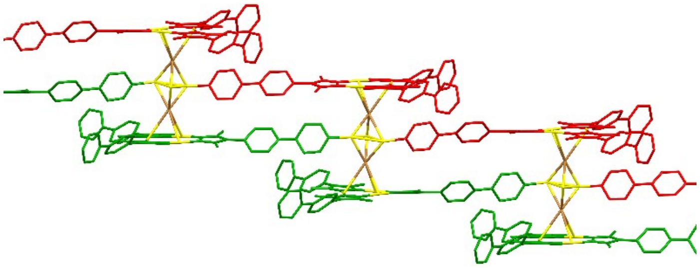


Figure S5. Extended structure of MOF 1, illustrating the double linkage between two neighbouring sandwich units and the how the units propagate upward and downward (only three sandwich repeating units are shown for clarity).

As shown in Fig. S5, two neighboring sandwich repeating units are doubly linked together through the coordination of a pyridine nitrogen donor atom of one unit to a Cu^I centre in the middle of the other unit. Each sandwich repeating unit is linked with six neighbouring ones around itself through the double linkage described above. Three of these six units are propagating upward and the remaining three downward with respect to the central sandwich unit in an alternating manner.

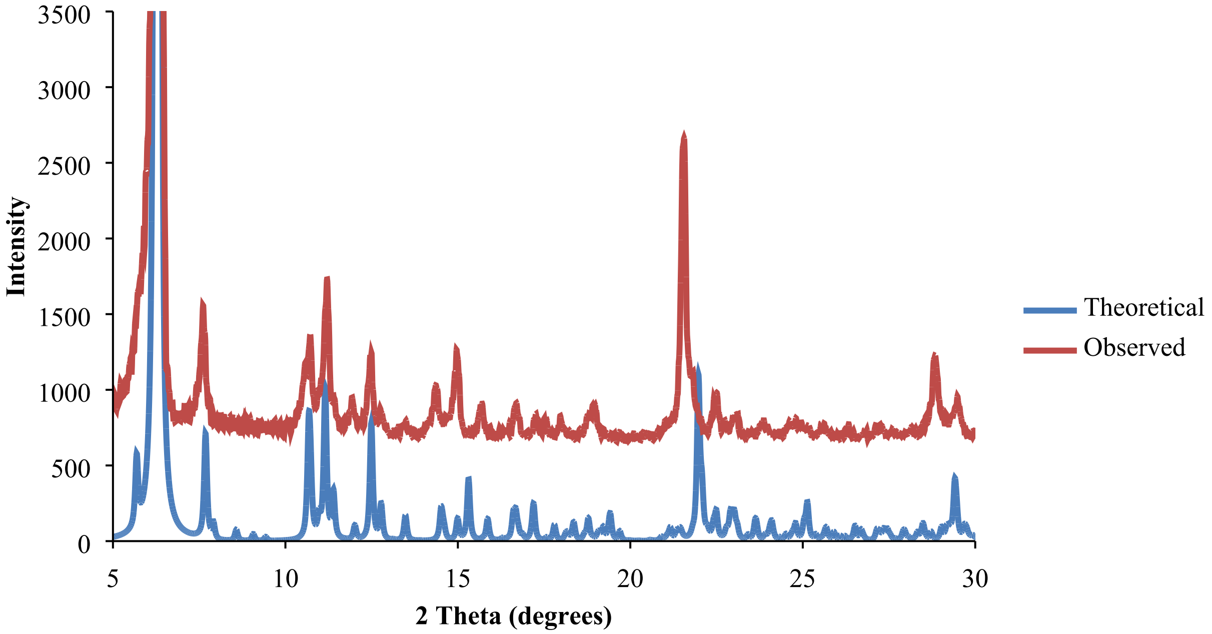


Figure S6. Theoretical versus observed PXRD spectrum for **1**

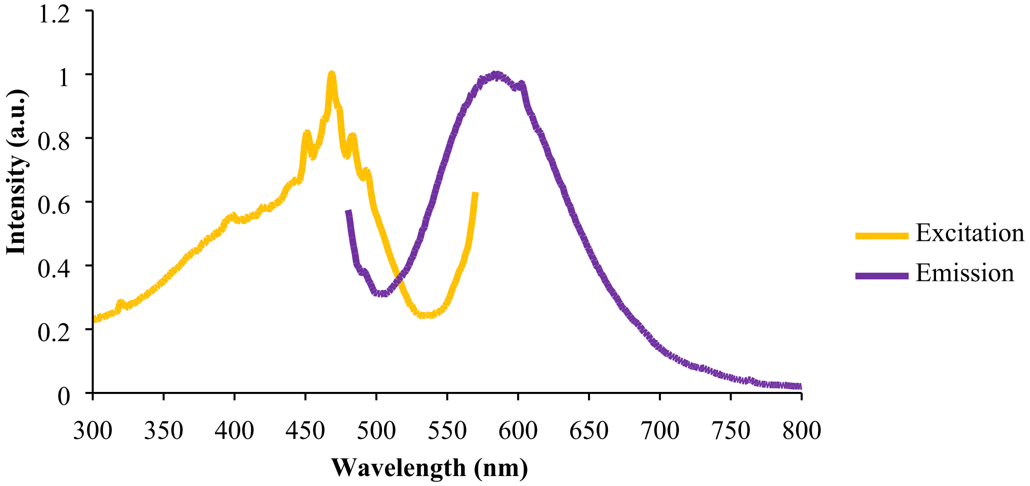


Figure S7. Averaged excitation (with detection at 582 nm) and emission (with excitation at 468 nm) spectra of a bulk sample of vacuum dried **1**.

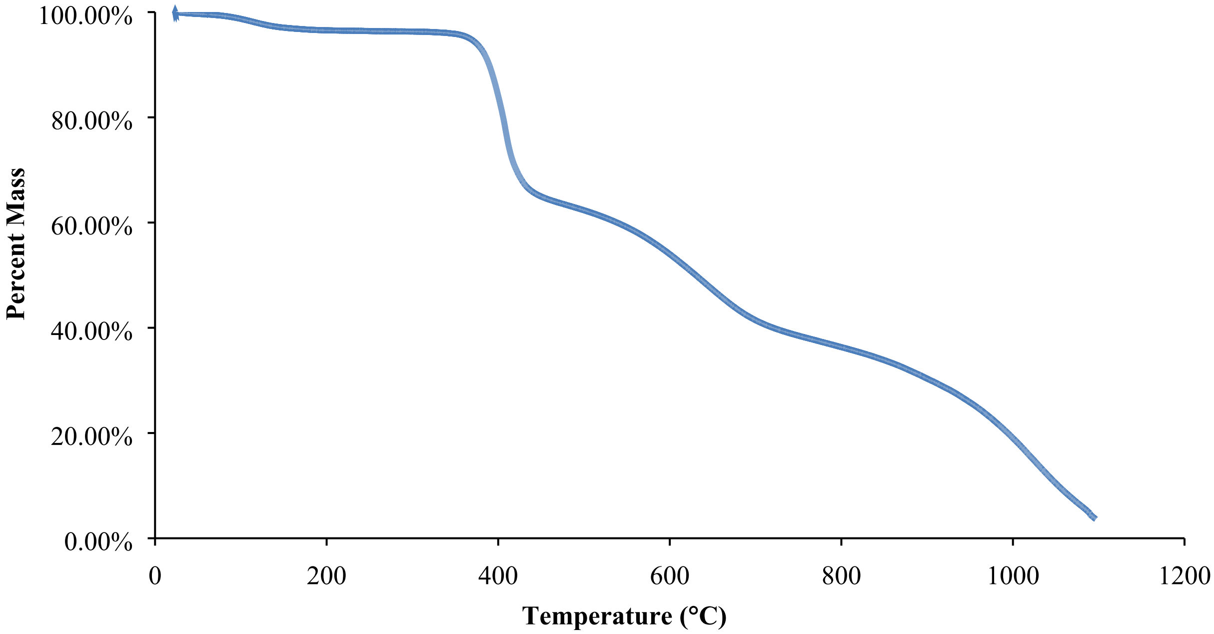


Figure S8. Mass change upon heating **1** treated with water vapour for 24 hours. There is a 3.5% mass loss (assigned as pore water) between 40 and 200 °C with the greatest mass loss occurring between 100 and 140 °C . Structure decomposition begins at ~360 °C.

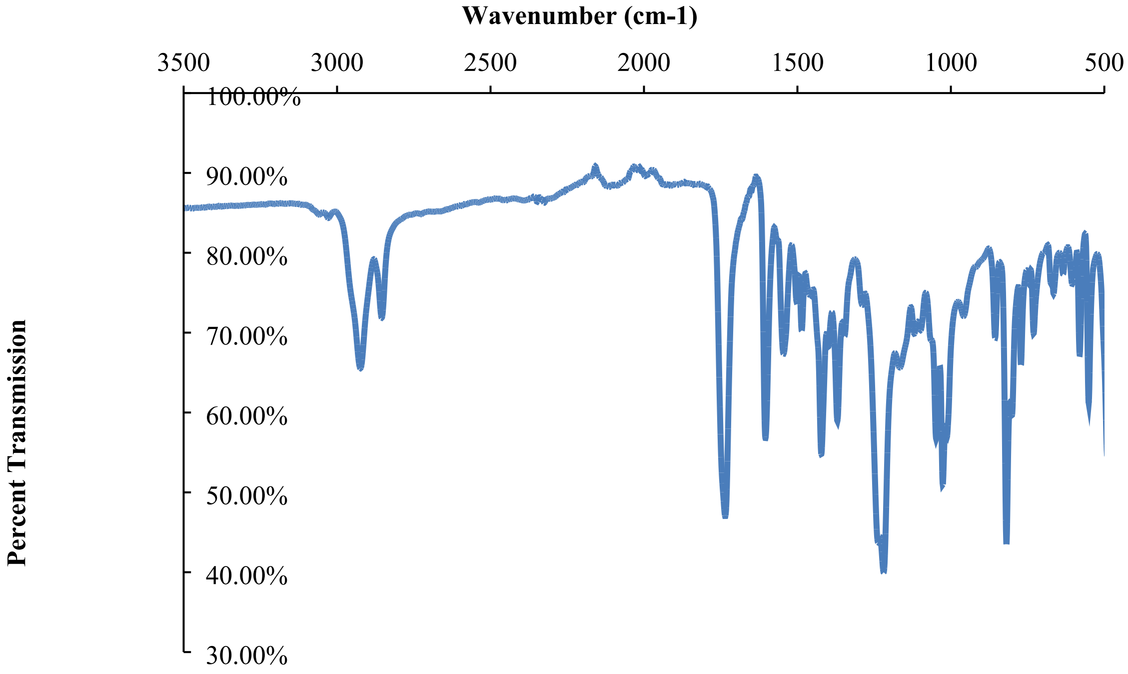


Figure S9. Infrared spectrum of neat sample of **1**.

X-Ray Procedures:

X-ray quality single crystals of **1** were obtained as described in the synthesis above. The crystal of **1** was mounted on the tip of a MiTeGen MicroMount. The single-crystal X-ray diffraction data were collected on a Bruker Kappa Apex II CCD diffractometer with Mo Kα radiation (λ = 0.71073 Å) operating at 50 kV and 30 mA, at 150 K controlled by an Oxford Cryostream 700 series low temperature system. The data integration and absorption correction were performed with the Bruker Apex 2 software package.[3] The structure was solved by direct methods and refined using SHELXTL V6.14.[4,5] Disordered solvent molecules and residual electron density were removed using the Platon Squeeze method.[6] All non-hydrogen atoms except for the atoms involved in the disordered portions were refined anisotropically. The positions of the hydrogen atoms were calculated using the riding model.

Table S1. Crystallographic properties of **1**

Formula	$C_{96}H_{84}Br_4Cu_{10}N_{18}$
Formula Weight [g/mol]	2444.85
Crystal System	Monoclinic
Space Group	C2/c (No. 15)
a [Å]	19.6076(13)
b [Å]	27.6940(16)
c [Å]	21.551(2)
alpha	90
beta	107.054(2)
gamma	90
Volume [Å^3]	11187.9(14)
Z	4
D(calc) [g/cm^3]	1.452
Mu(MoKa) [/mm]	3.336
F(000)	4864
Crystal Size (estimated) [mm]	0.02 x 0.06 x 0.08
Temperature (K)	150
Radiation [Angstrom	MoKa: 0.71073
Theta Min-Max [Deg]	1.8, 27.5
Dataset	-25: 25 ; -35: 35 ; -27: 28
Tot., Uniq. Data, R(int)	61644, 12861, 0.070
Observed data [I > 2.0 sigma(I)]	8030
Nref, Npar	12861, 606
R, wR$_2$, GooF	0.0666, 0.1899, 1.04
Max. and Av. Shift/Error	0.00, 0.00
Min. and Max. Resd. Dens. [e/Ang^3]	-1.20, 1.94

$$R_1 = \frac{\sum (F_o - F_c)}{\sum F_o} \qquad wR_2 = R_w(F^2) = \sqrt{\frac{\sum w\left(F_o^2 - F_c^2\right)^2}{\sum w\left(F_o^2\right)^2}}$$

MOF Properties and Performance:

<u>PXRD Investigation of Structure-Activity Relationship – Cycling of Water and Solvent Vapour</u>:

An ethyl acetate dropcast sample of **1** was prepared on a zero background sample holder. The sample holder was placed in a degassed, sealed 250 mL flask with a septum and protected from light. Solvent vapour, using nitrogen as a carrier gas, was diffused into the flask for the listed time. If the previous solvent was water, additional diffusion time was necessary (e.g. EtOAc after 42 hours still showed trace water present (Fig S9)).

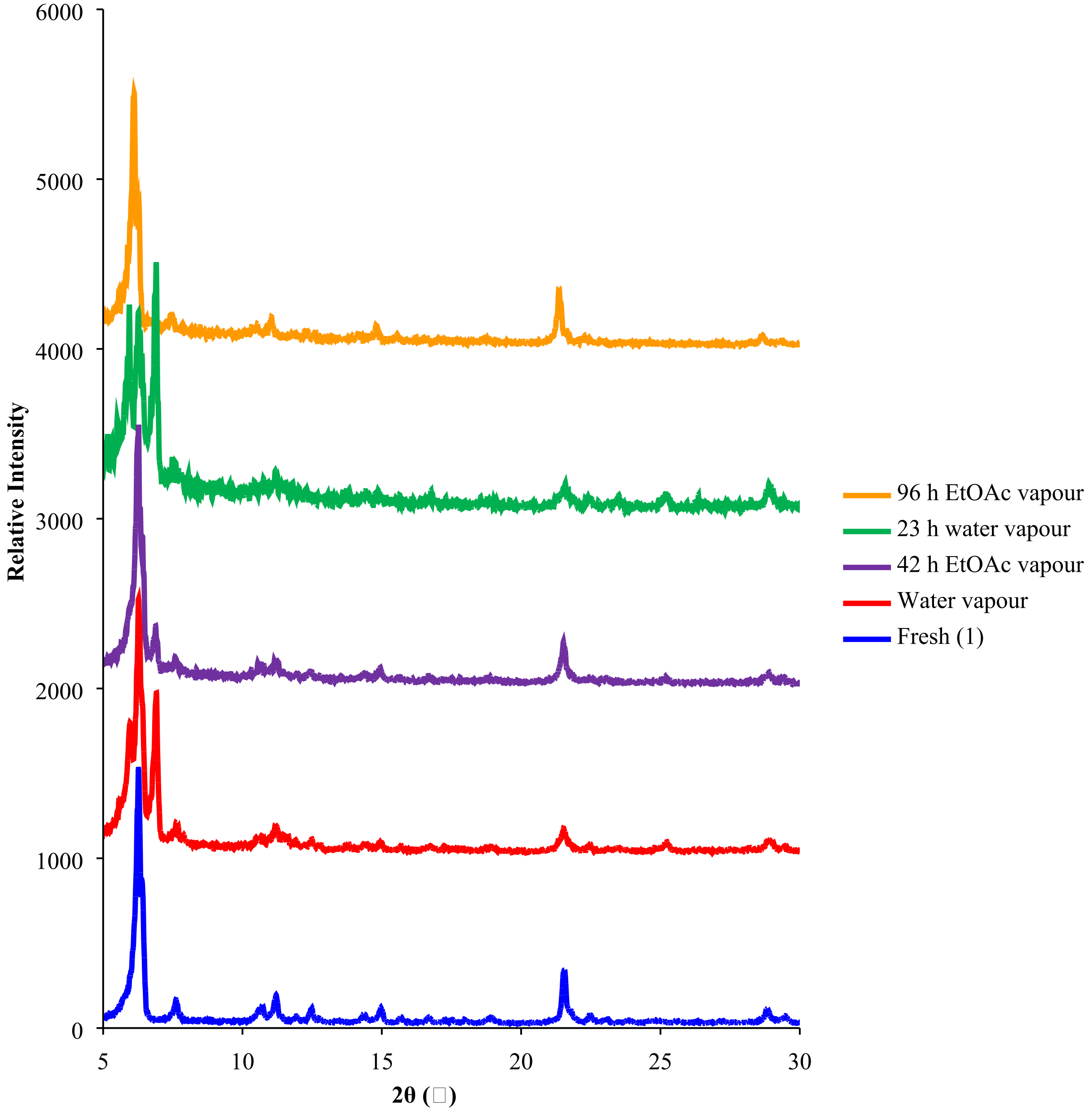


Figure S10. PXRD comparison of freshly made **1** (blue) sequentially treated with water vapour (red), ethyl acetate vapour (purple), water vapour (green), and ethyl acetate vapour (orange). Note loss of major peaks at 6.11°, 6.29° and the emergence of a new peak at 6.90° upon water exposure.

PXRD Investigation of Structure-Activity Relationship – Structural Changes of Water vs Solvent Vapour:

A bulk sample of **1** was exposed to 19+ hours of water vapour before being drop cast with acetone on a zero background sample holder to establish a water baseline. Bulk, water treated **1** was then divided into vials, placed into degassed, septum sealed 16 mm x 150 mm test tubes and protected from light. Solvent vapour, using nitrogen as a carrier gas, was then diffused into the various test tubes at a rapid rate for 18+ hours. After solvent exposure, the samples of **1** were drop cast on a zero background sample holder using the analyte solvent for comparison with the water baseline.

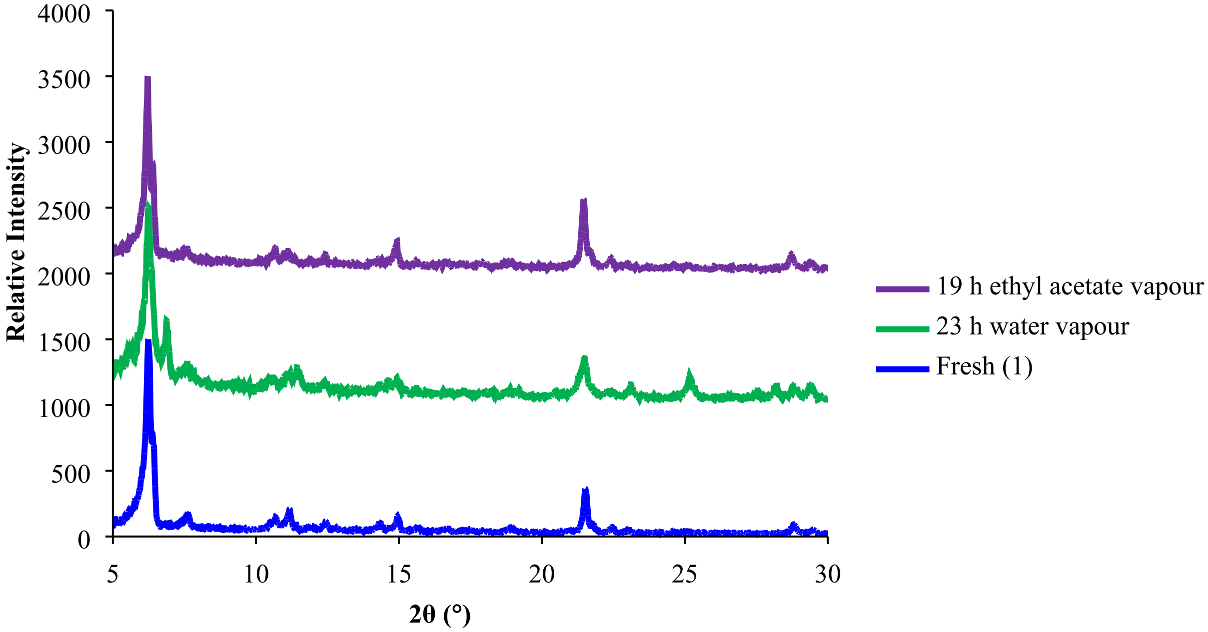


Figure S11. PXRD comparison of fresh **1** (blue), water vapour treated **1** (green), and subsequent treatment with ethyl acetate vapour (purple).

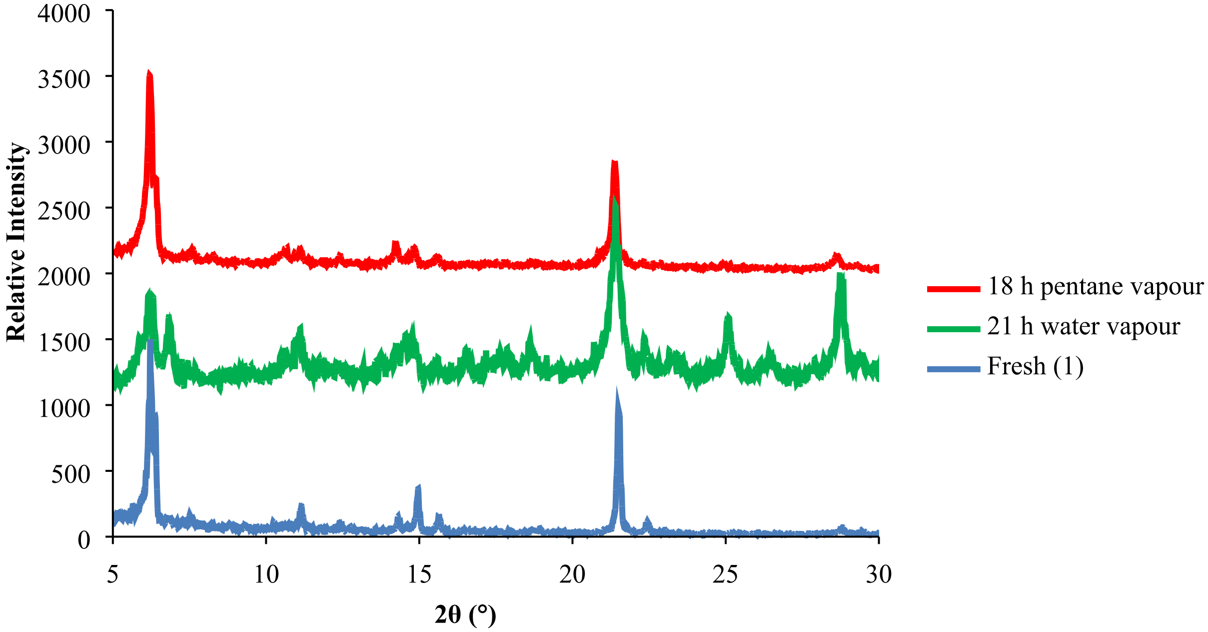


Figure S12. PXRD comparison of fresh **1** (blue), water vapour treated **1** (green), and subsequent treatment with pentane vapour (red).

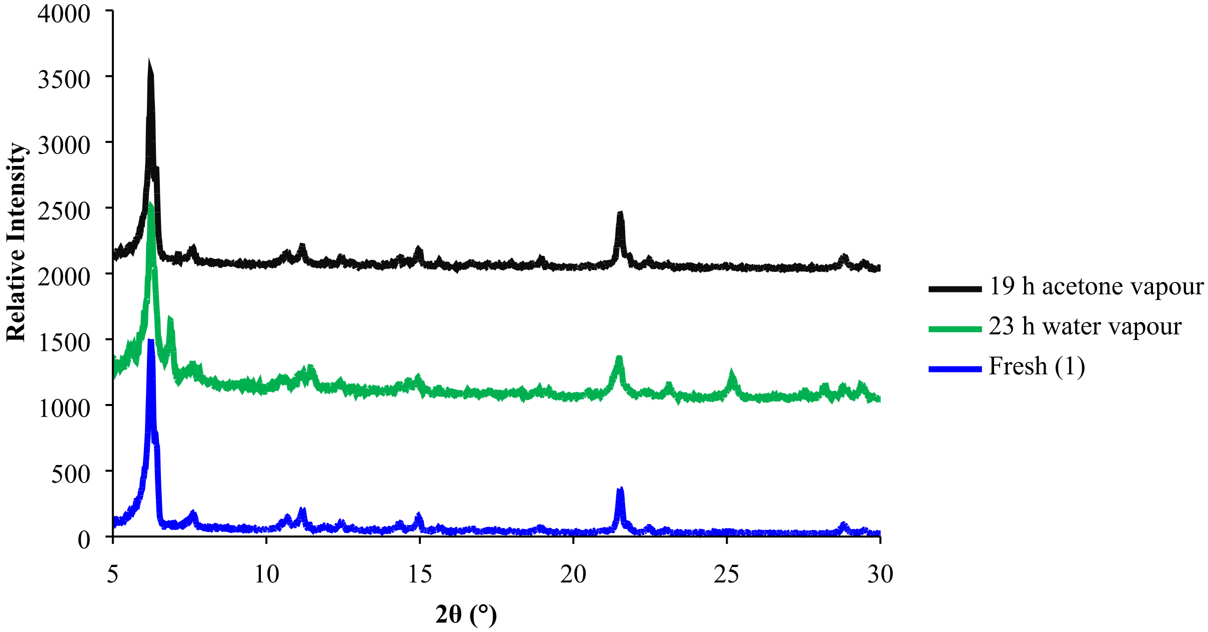


Figure S13. PXRD comparison of fresh **1** (blue), water vapour treated **1** (green), and subsequent treatment with acetone vapour (black).

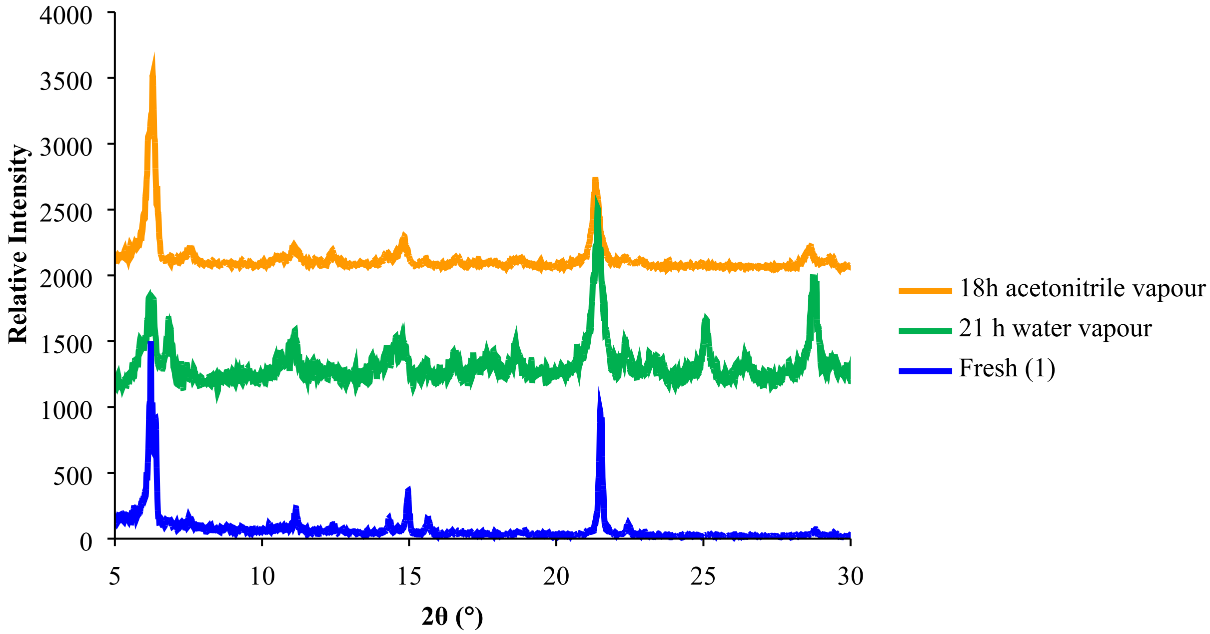


Figure S14. PXRD comparison of fresh **1** (blue), water vapour treated **1** (green), and subsequent treatment with acetonitrile vapour (orange).

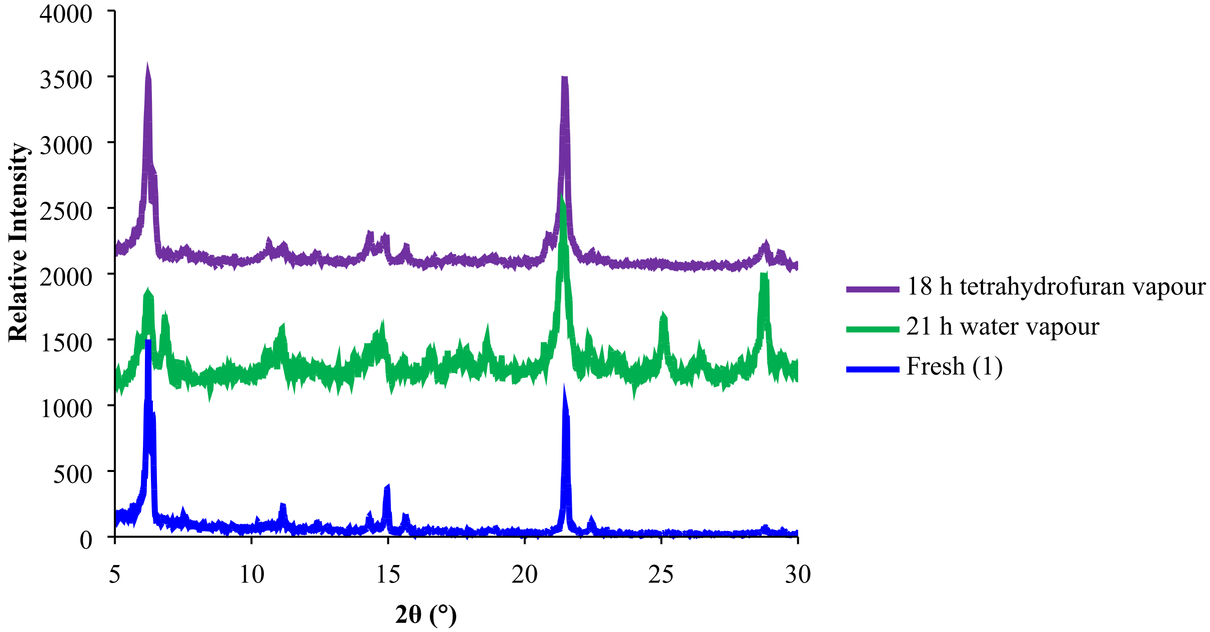


Figure S15. PXRD comparison of fresh **1** (blue), water vapour treated **1** (green), and subsequent treatment with tetrahydrofuran vapour (purple).

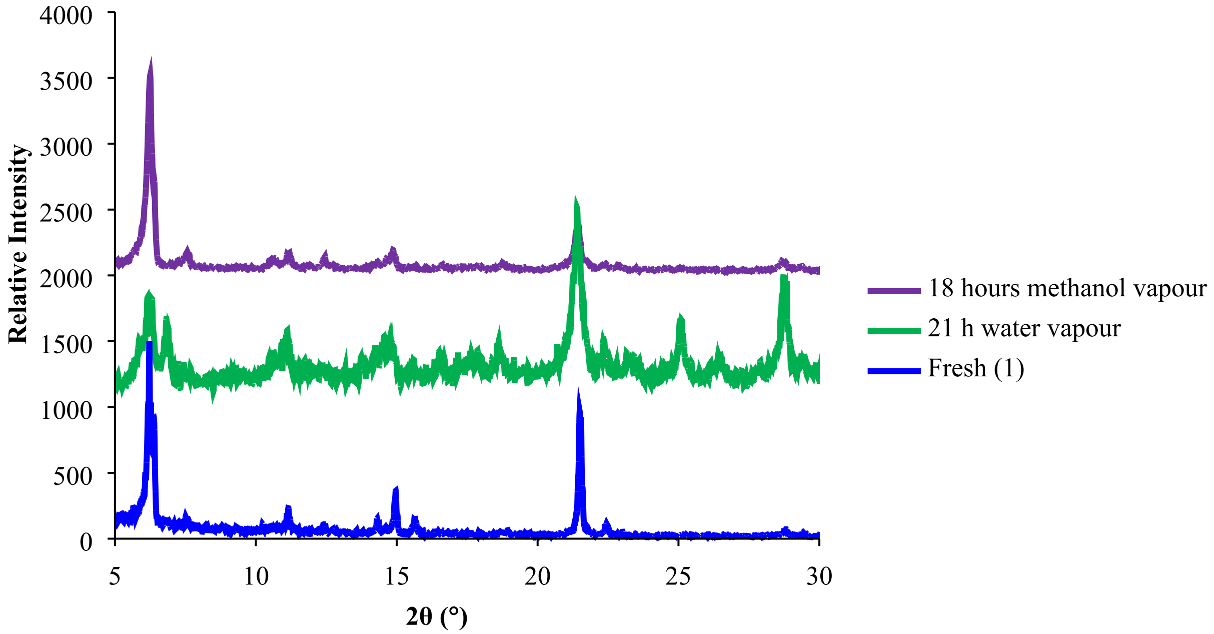


Figure S16. PXRD comparison of fresh **1** (blue), water vapour treated **1** (green), and subsequent treatment with methanol vapour (grey).

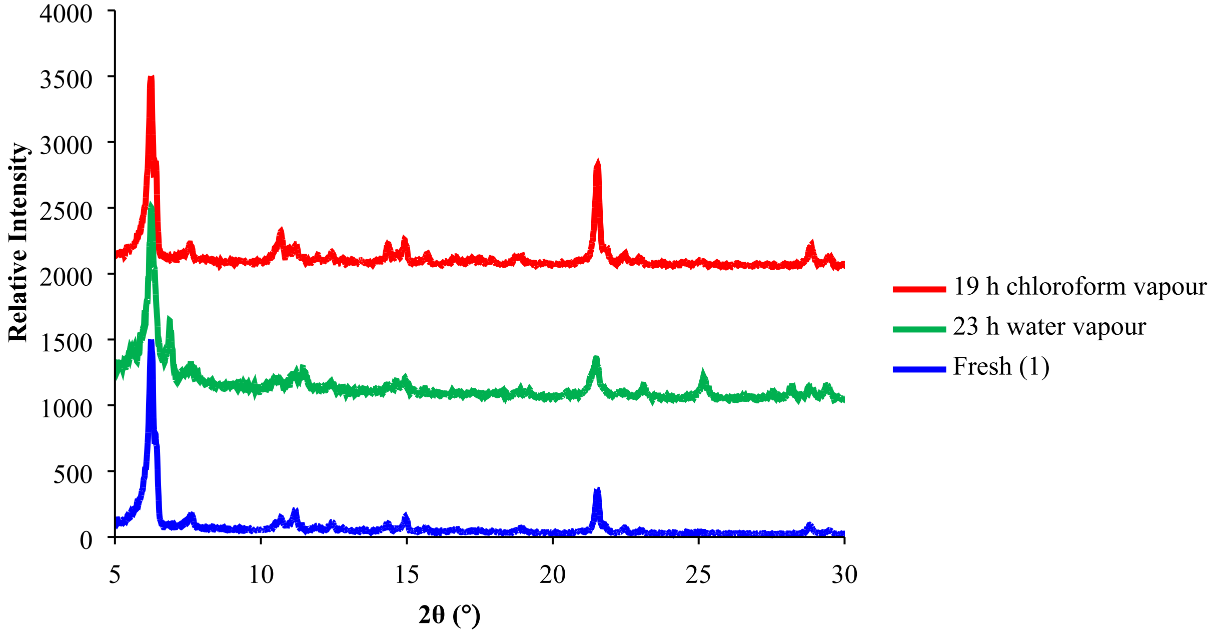


Figure S17. PXRD comparison of fresh **1** (blue), water vapour treated **1** (green), and subsequent treatment with chloroform vapour (red).

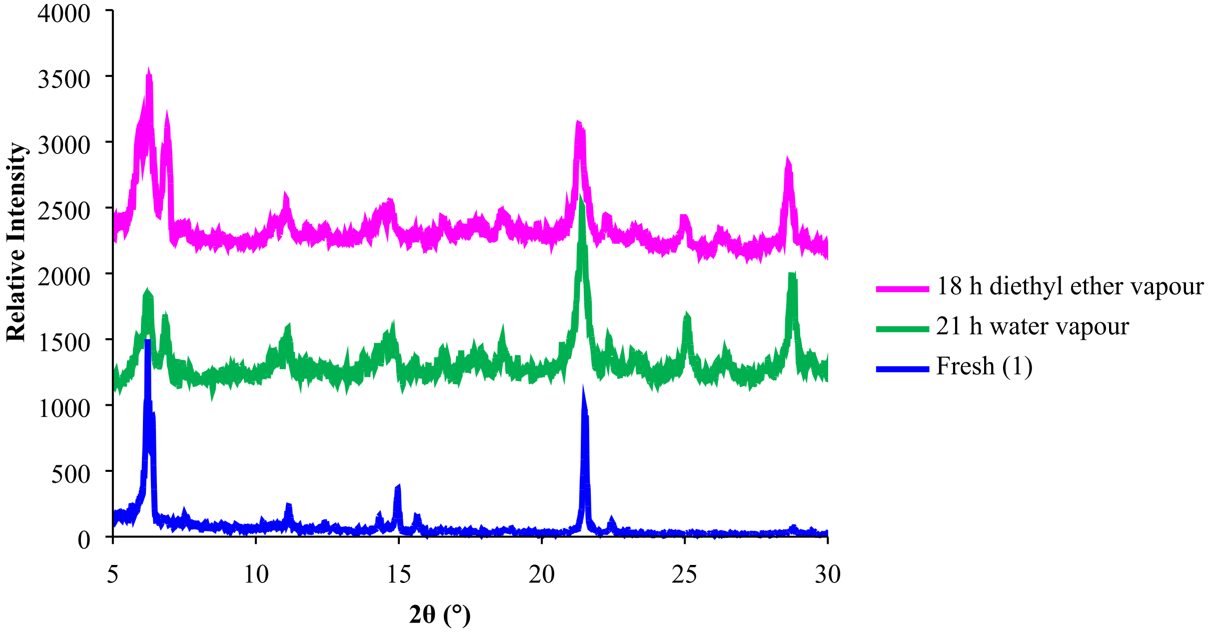
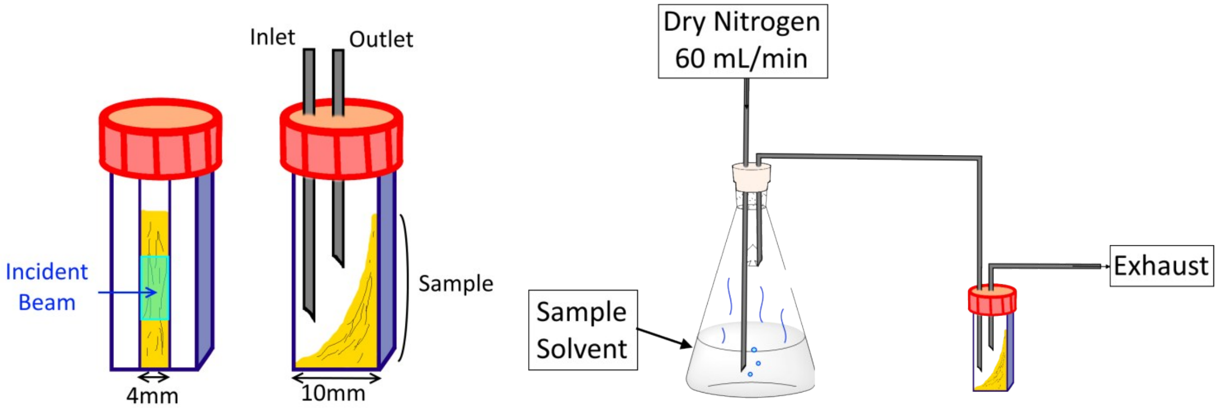
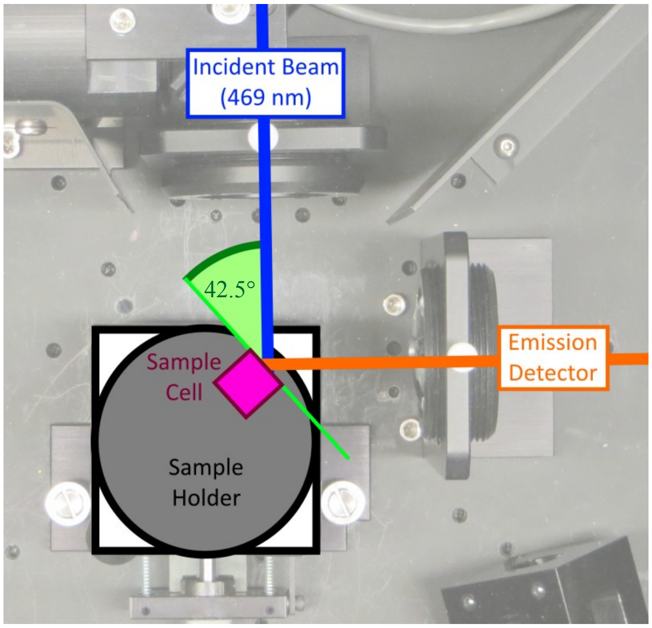


Figure S18. PXRD comparison of fresh **1** (blue), water vapour treated **1** (green), and subsequent treatment with diethyl ether vapour (pink).

Description of Luminescent Experimental Procedure:



Scheme S2. Cuvette and VOC exposure setup for luminescent gas sensing experiments



Scheme S3. Configuration of luminescence spectrometer for luminescent gas sensing experiments

1 was loaded into a 4 mm wide quartz cuvette until the viewing window was covered by free-flowing material (~150 mg) and fitted with a screw-top cap containing a plastic septum. A water vapour baseline was established by bubbling nitrogen through distilled water at a rate of 60 mL/min and introducing it to the cuvette via needles (Scheme S2). The needles were removed and the luminescence spectrum measured (Scheme S3). The cuvette was then agitated to display a fresh sample surface and the measurements were repeated a minimum of seven times (total). In this way, the average baseline response of the material may be recorded.

1 was then exposed to VOC vapour following the same procedure. The MOF is periodically monitored until there is no intensity change between measurements (sample is saturated with solvent vapour). Saturation time was highly dependent on the vapour pressure of the VOC. Once saturated, seven measurements were taken by again agitating the cuvette between measurements to collect the average luminescence of **1**.

After every VOC solvent gas, **1** was regenerated by extended vacuum (≥48 hours). If shorter durations or other methods are used VOC may remain and skew subsequent measurements. Regeneration is judged effective if the water baseline closely matches that of the previous sample.

VOC Sensing Results:

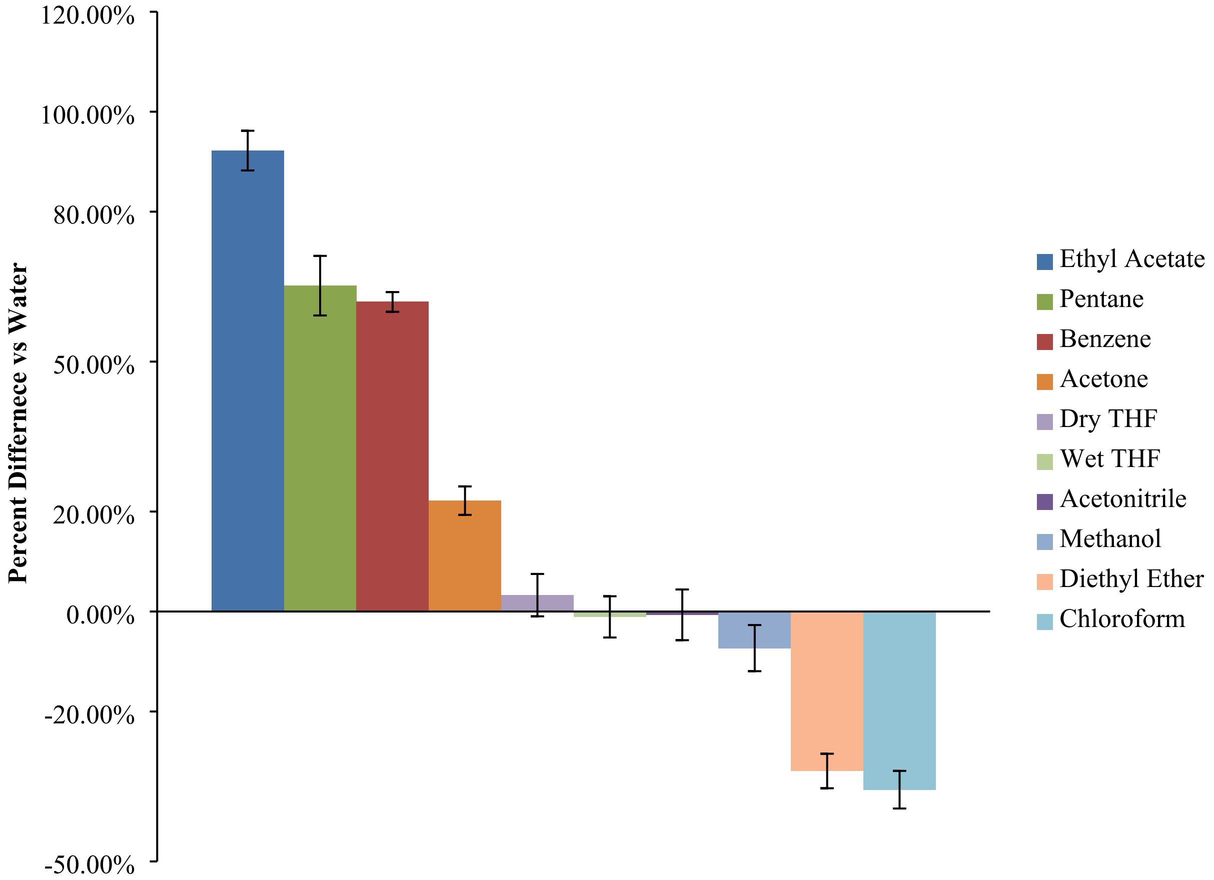


Figure S19. VOC sensing results measured as percent difference compared to water-treated **1**. Excitation wavelength is 469 nm and response is monitored at the emission maxima of each solvent (Table S2). Errors are +/- one standard deviation.

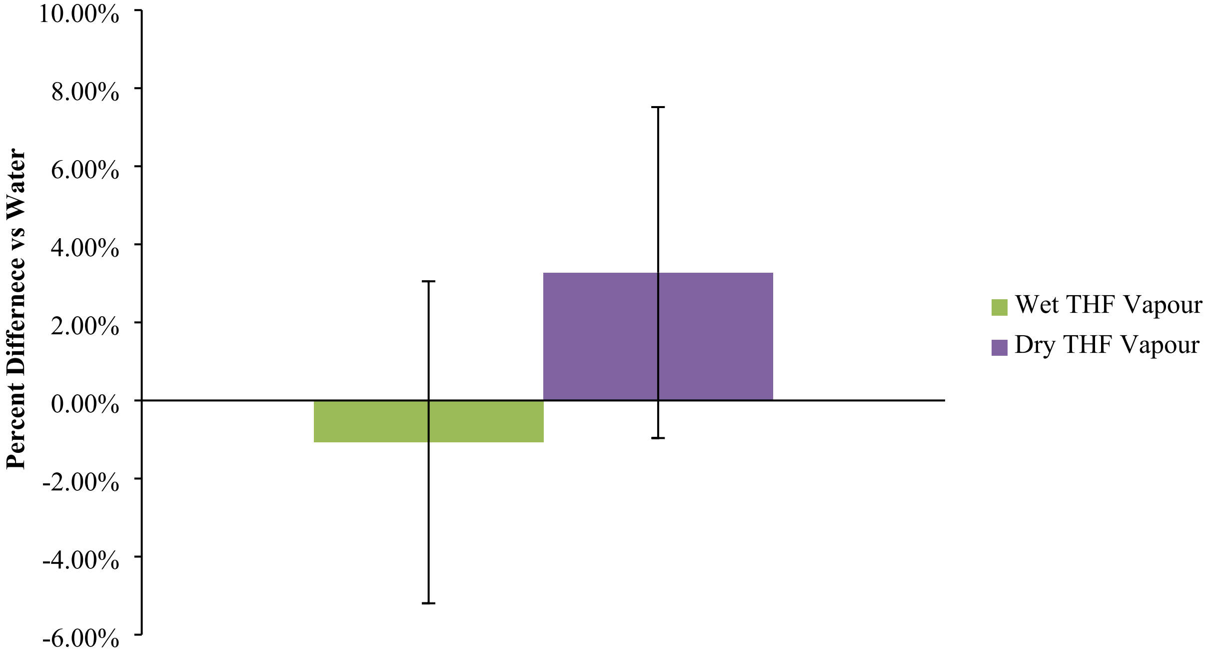


Figure S20. Sequential exposure of **1** to dry and wet THF following standard procedures. Sample illuminated at 469 nm and monitored at the peak emission of THF (559 nm).

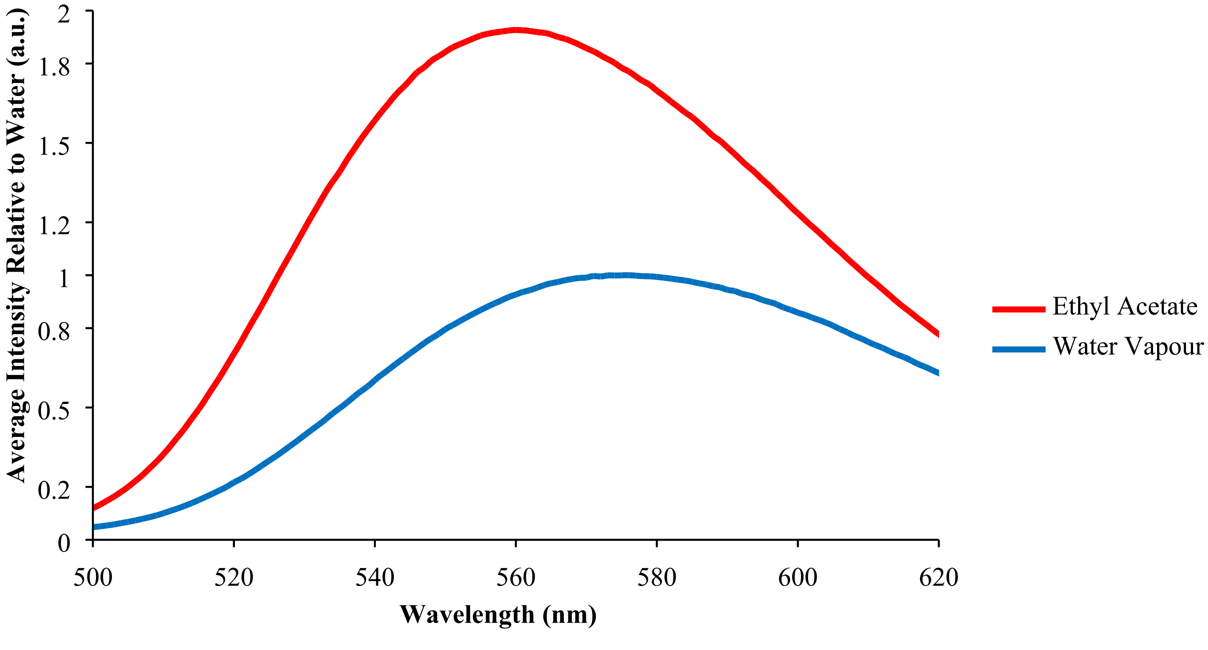


Figure S21. Averaged emission intensity of **1** after VOC treatment (ethyl acetate – red) relative to averaged pre-exposure water vapour emission (blue) using an excitation wavelength of 469 nm.

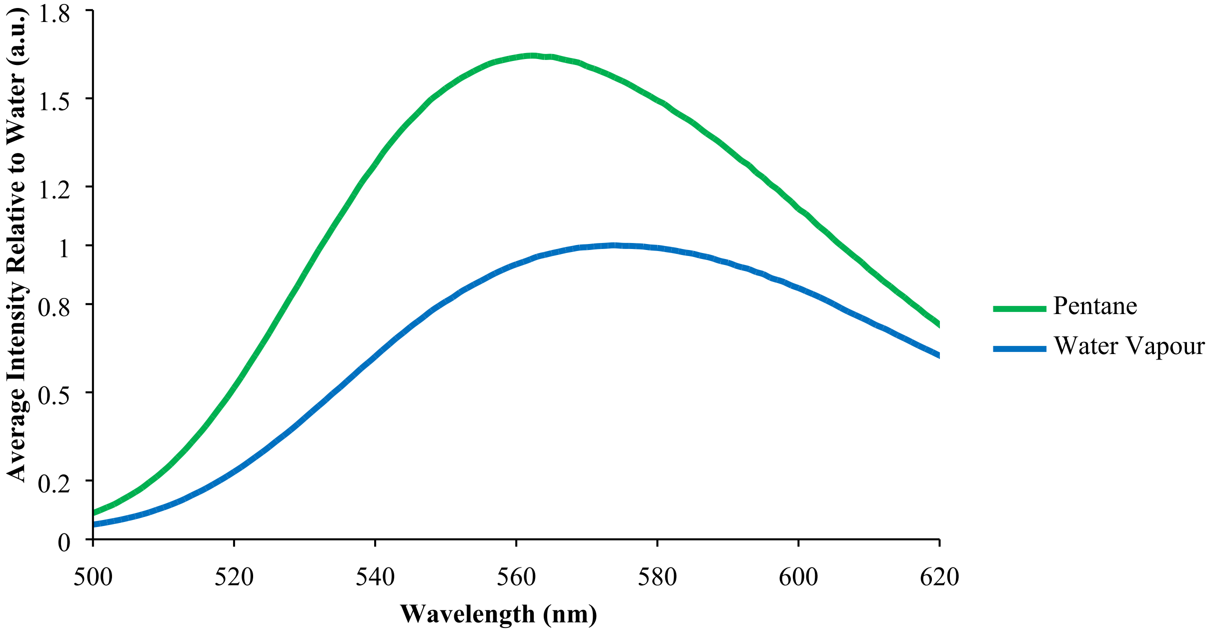


Figure S22. Averaged emission intensity of **1** after VOC treatment (pentane – green) relative to averaged pre-exposure water vapour emission (blue) using an excitation wavelength of 469 nm.

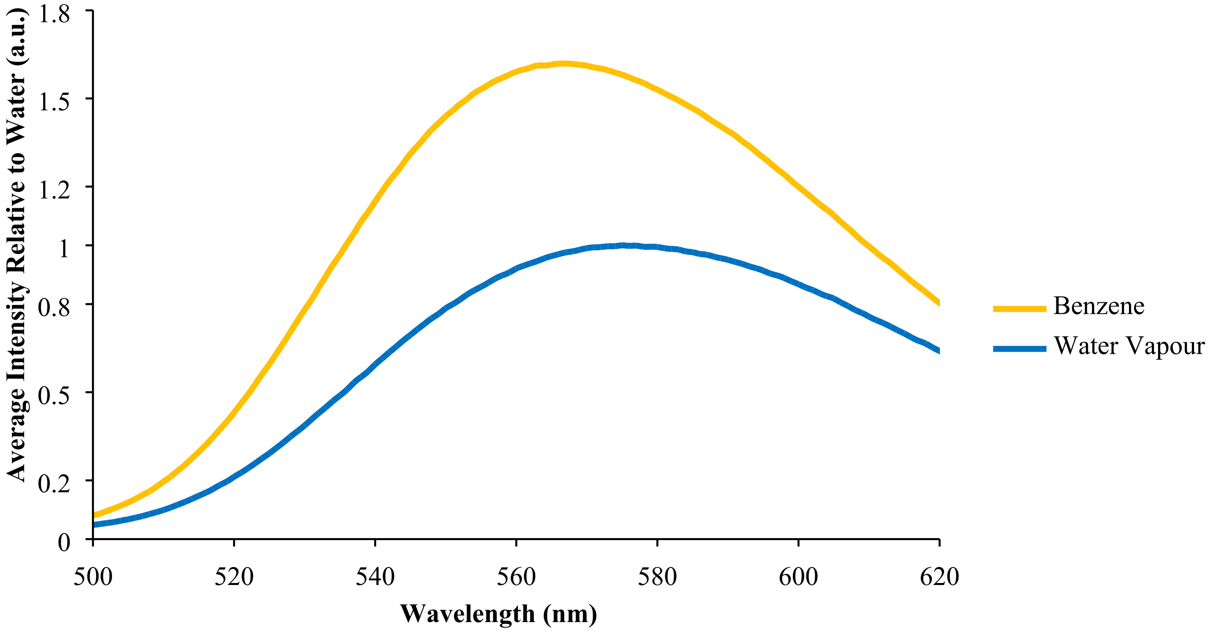


Figure S23. Averaged emission intensity of **1** after VOC treatment (benzene – orange) relative to averaged pre-exposure water vapour emission (blue) using an excitation wavelength of 469 nm.

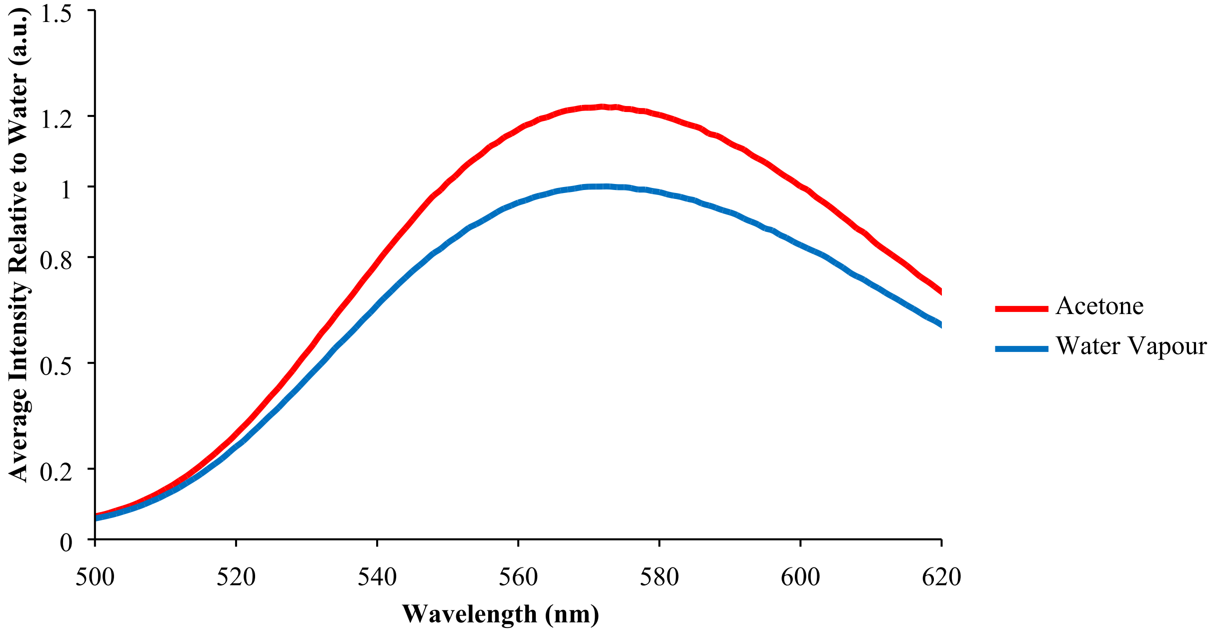


Figure S24. Averaged emission intensity of **1** after VOC treatment (acetone – red) relative to averaged pre-exposure water vapour emission (blue) using an excitation wavelength of 470 nm.

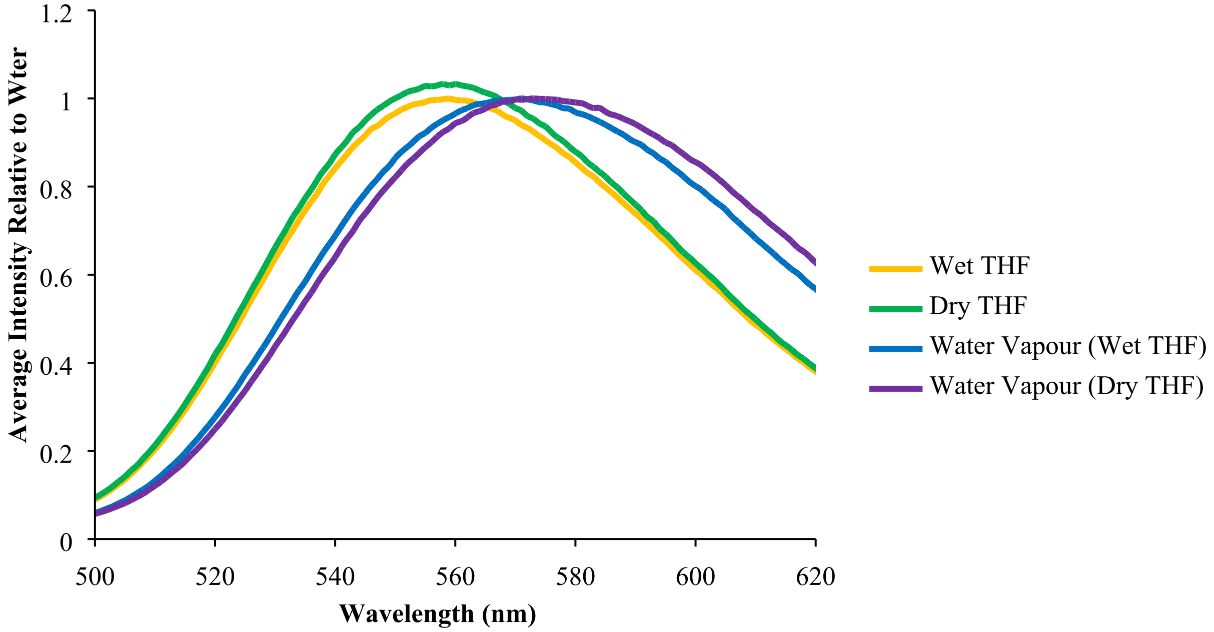


Figure S25. Averaged emission intensity of **1** after VOC treatment (wet THF – orange, dry THF - green) relative to averaged pre-exposure water vapour emission (blue for wet THF, purple for dry THF) using an excitation wavelength of 470 nm.

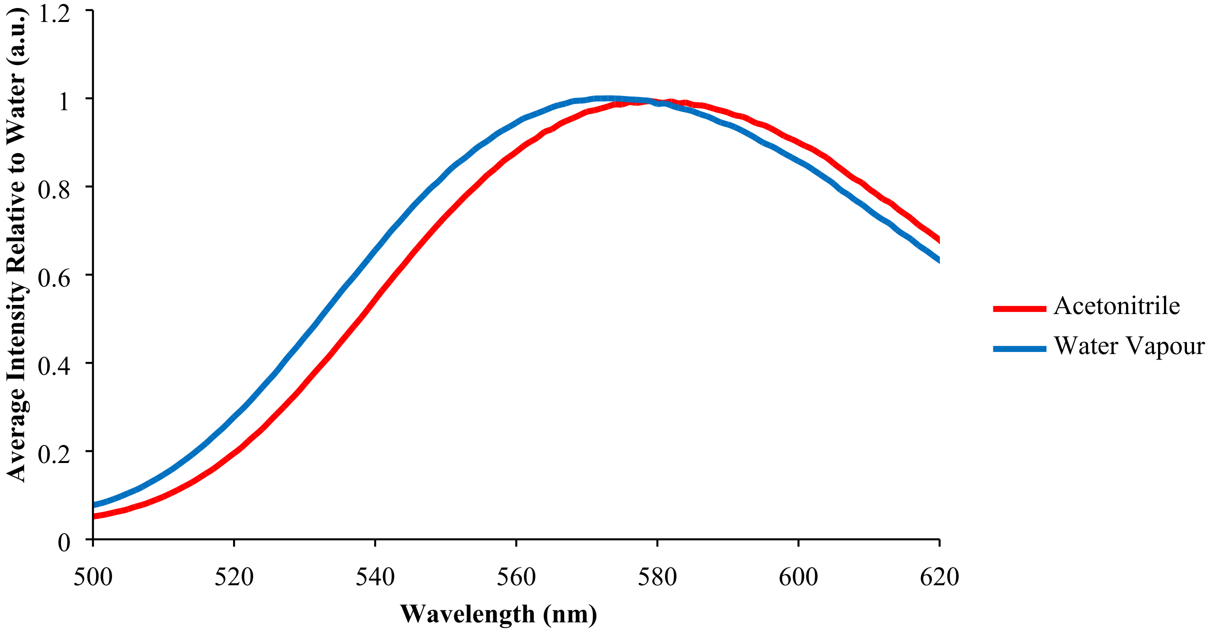


Figure S26. Averaged emission intensity of **1** after VOC treatment (acetonitrile – red) relative to averaged pre-exposure water vapour emission (blue) using an excitation wavelength of 469 nm.

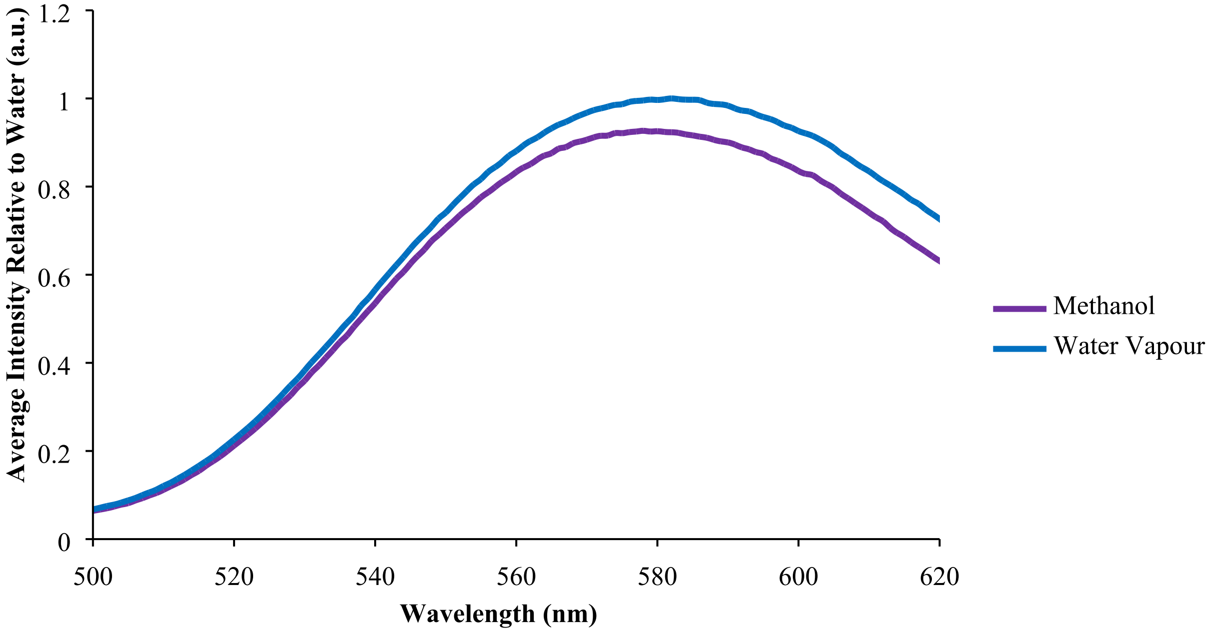


Figure S27. Averaged emission intensity of **1** after VOC treatment (methanol – purple) relative to averaged pre-exposure water vapour emission (blue) using an excitation wavelength of 470 nm.

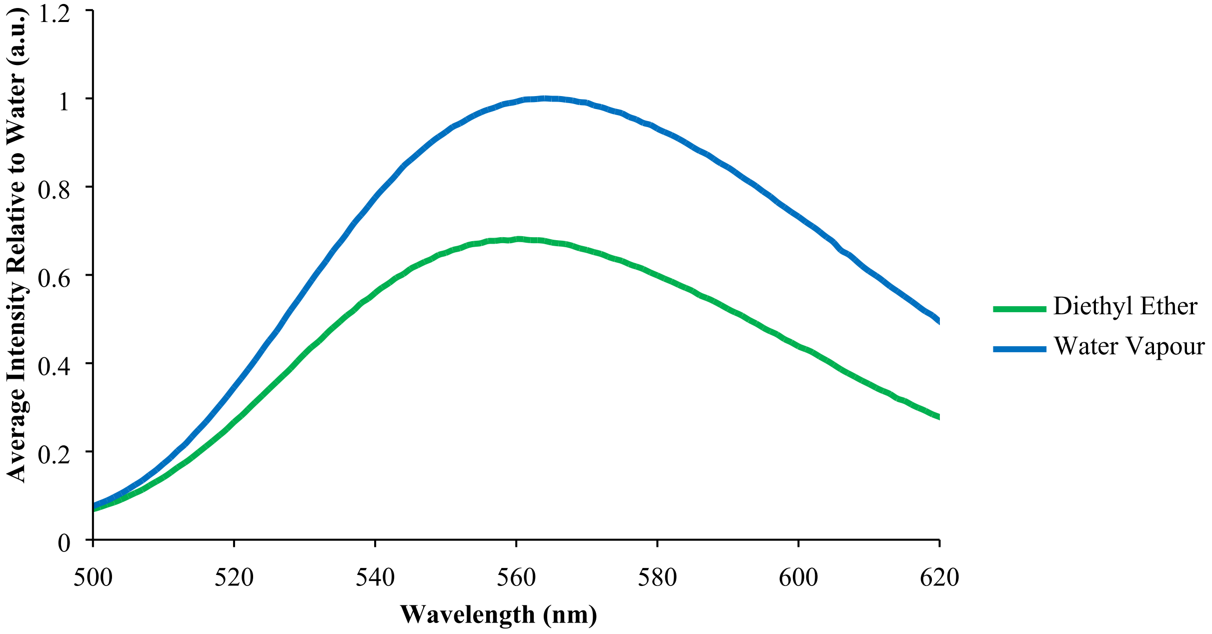


Figure S28. Averaged emission intensity of **1** after VOC treatment (diethyl ether – green) relative to averaged pre-exposure water vapour emission (blue) using an excitation wavelength of 470 nm.

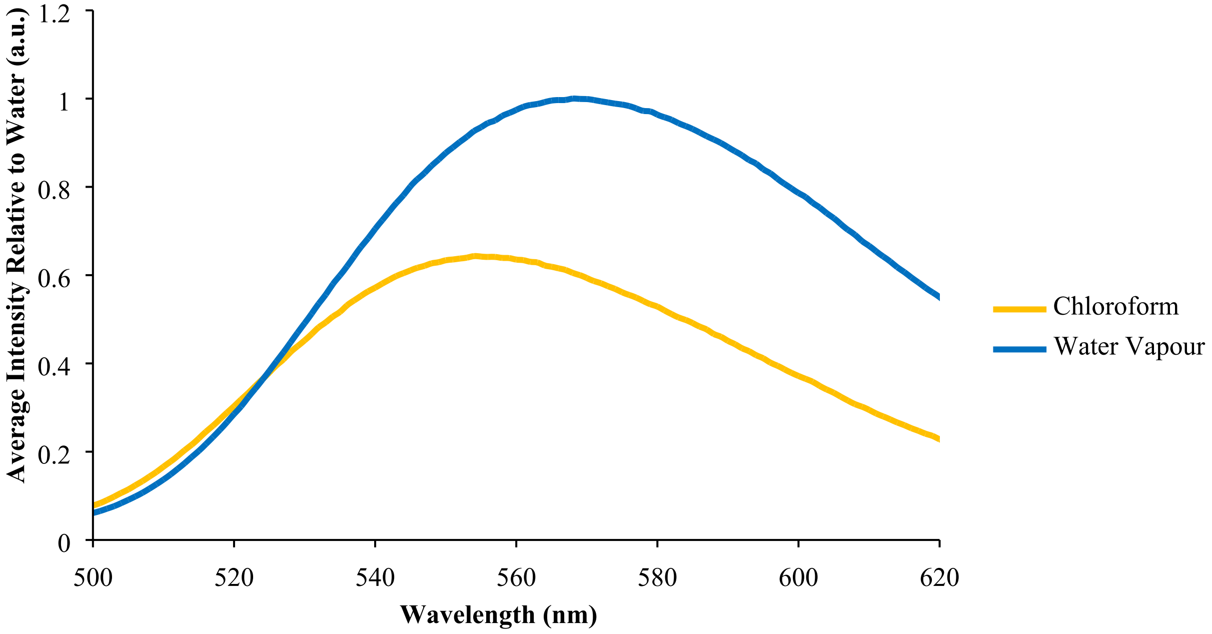


Figure S29. Averaged emission intensity of **1** after VOC treatment (chloroform - orange) relative to averaged pre-exposure water vapour emission (blue) using an excitation wavelength of 470 nm.

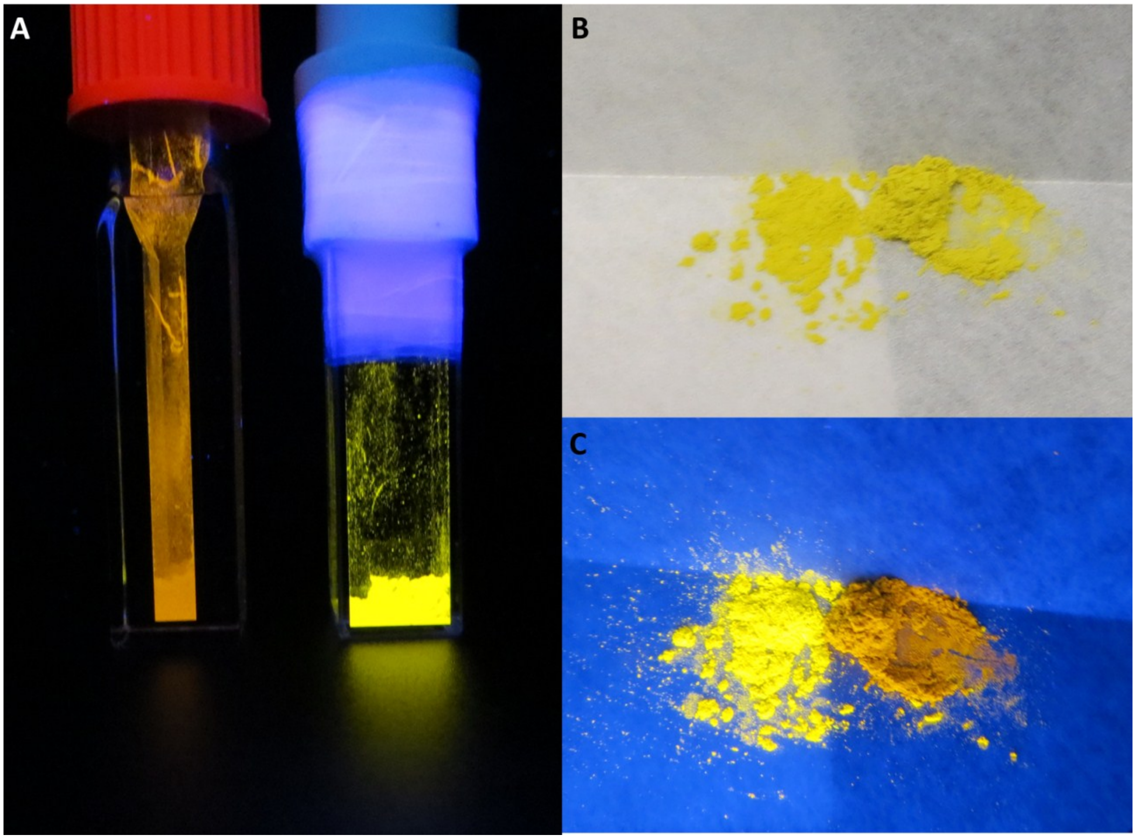


Figure S30. a) Visual comparisons of **1** exposed to water (left) and ethyl acetate vapour (right) for 30 min under nitrogen as viewed under a 365 nm UV lamp. Comparisons of powder samples post exposure under normal light (b) and a 365 nm UV lamp (c) on weigh paper. The water treated sample is on the right.

Table S2. Solvochromic effects on MOF luminescence over sequential experiments

	Max (nm)	**St Dev**
water	574.9	1.3
EtOAc	560.3	1.1
water	575.8	1.3
Benzene	566.7	1.0
water	573.6	2.4
Pentane	562.2	0.8
water	573.4	2.4
MeCN	579.3	1.4
water	577.6	2.4
THF	558.7	1.6
water	571.6	2.0
Acetone	572.9	1.2
water	582.2	2.5
MeOH	579.1	1.9
water	564.1	1.3
Et_2O	561.0	1.0
water	569.0	1.4
$CHCl_3$	554.9	1.1

Luminescence Lifetimes and Quantum Yields

Samples of **1** were tested under N_2 (as synthesized) or after 30 minutes of vapour diffusion (water or ethyl acetate with nitrogen as a carrier gas). All measurements were performed pseudo-air free on powdered samples in capped 1 cm quartz cuvettes.

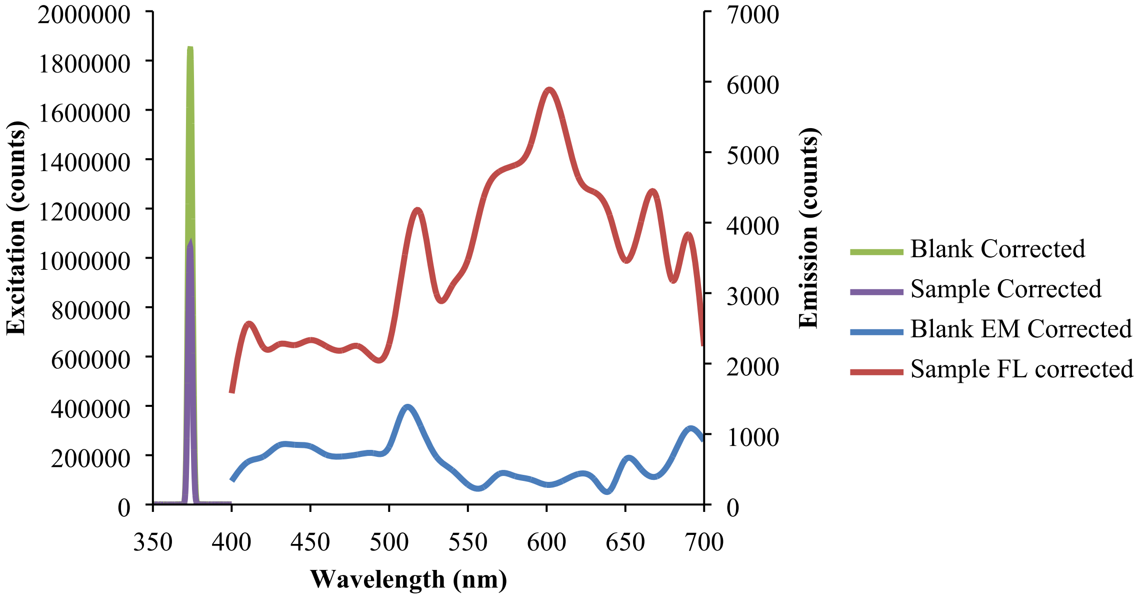


Figure S31. Spectra associated with quantum yield measurement of as-synthesized **1** with excitation at 375 nm.

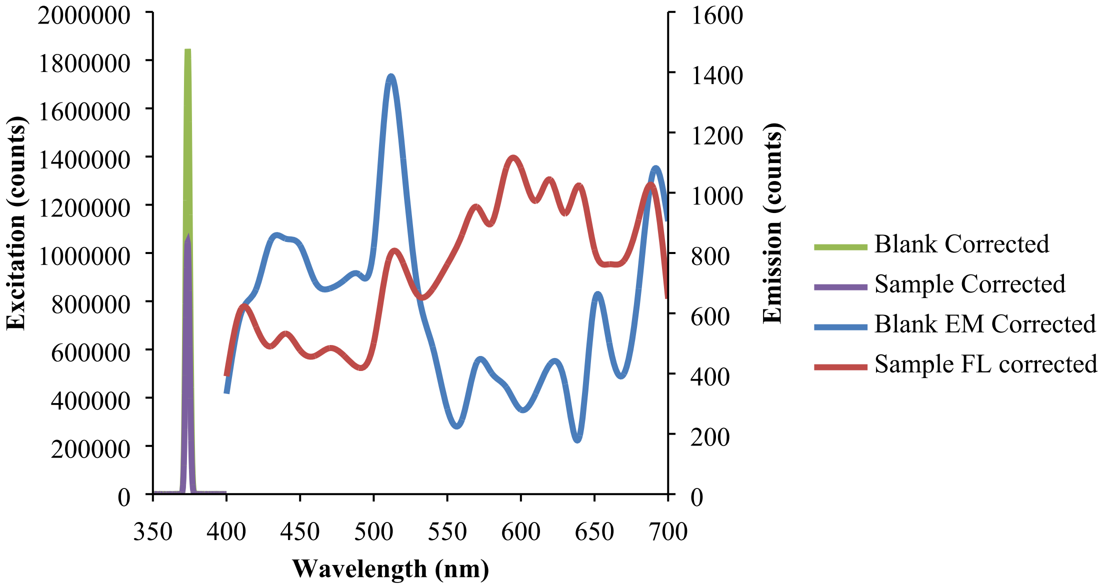


Figure S32. Spectra associated with quantum yield measurement of water vapour treated **1** with excitation at 375 nm.

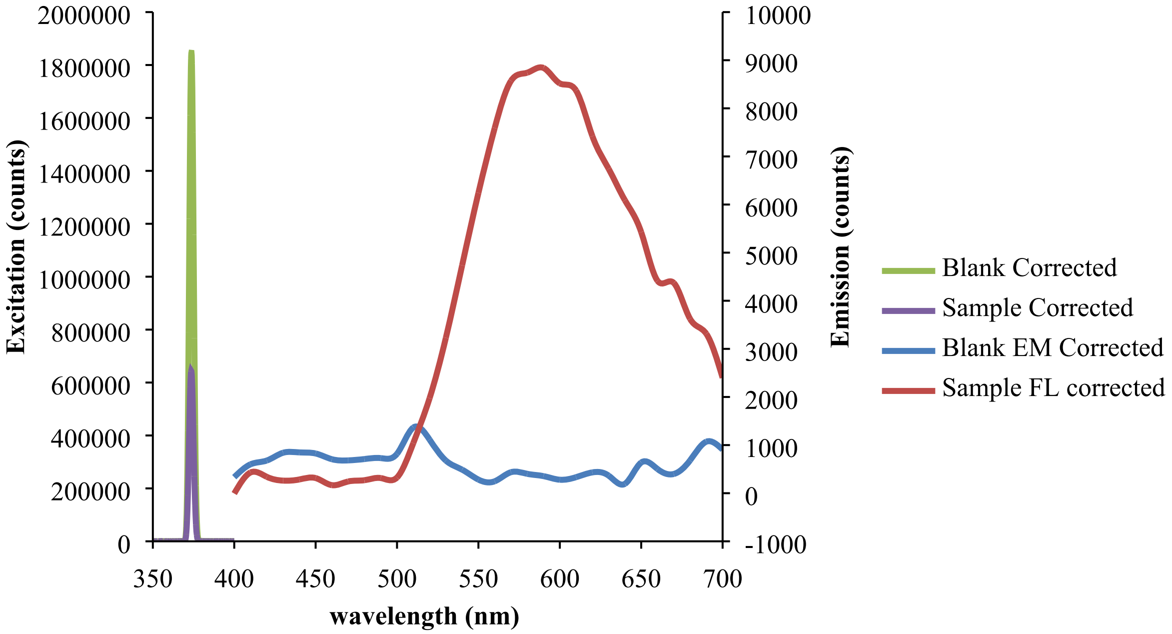


Figure S33. Spectra associated with quantum yield measurement of ethyl acetate vapour treated **1** with excitation at 375 nm.

Table S3. Results of Quantum Yield Measurements

	Quantum Yield (%)
As-synthesized (N_2)	8.6
Water Vapour	1.8
Ethyl Acetate Vapour	24.3

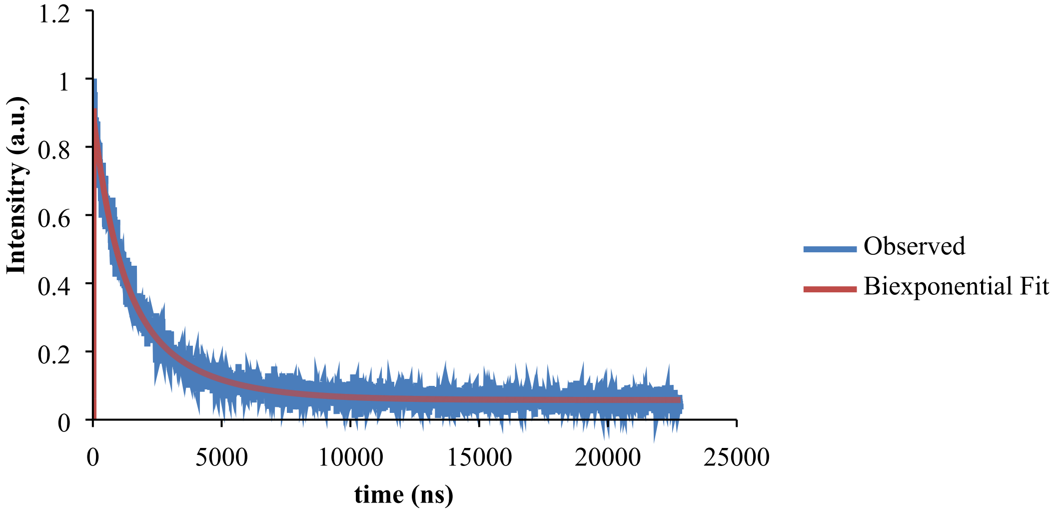


Figure S34. Observed luminescence decay for ethyl acetate treated **1** over 26 μs with a bi-exponential fit.

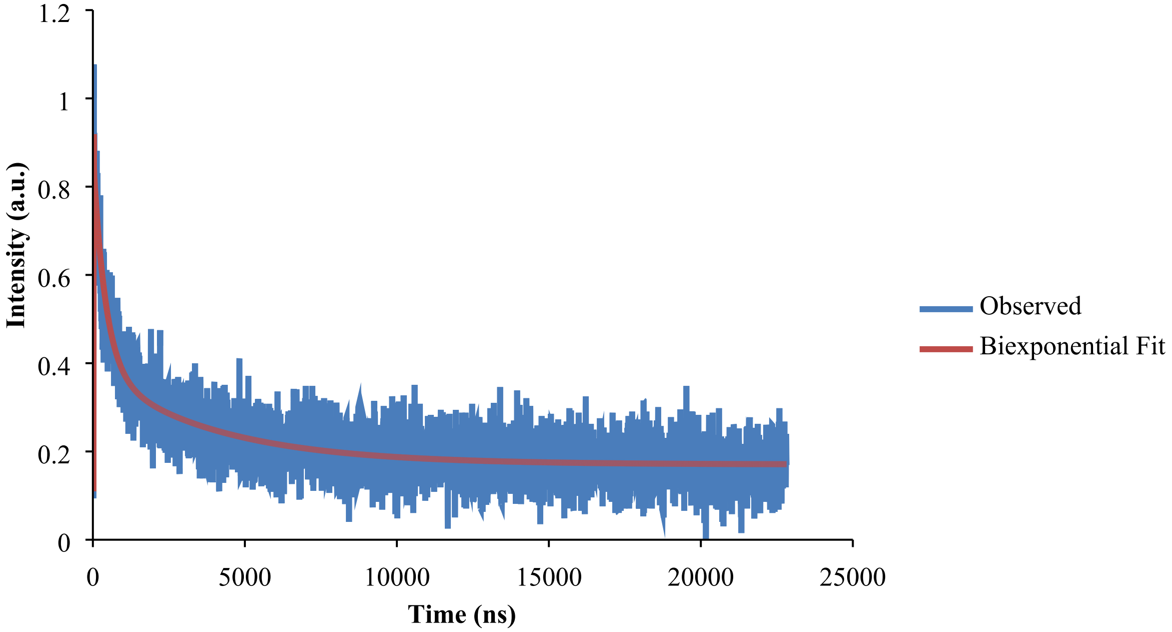


Figure S35. Observed luminescence decay for as-synthesized **1** over 26 μs with a bi-exponential fit.

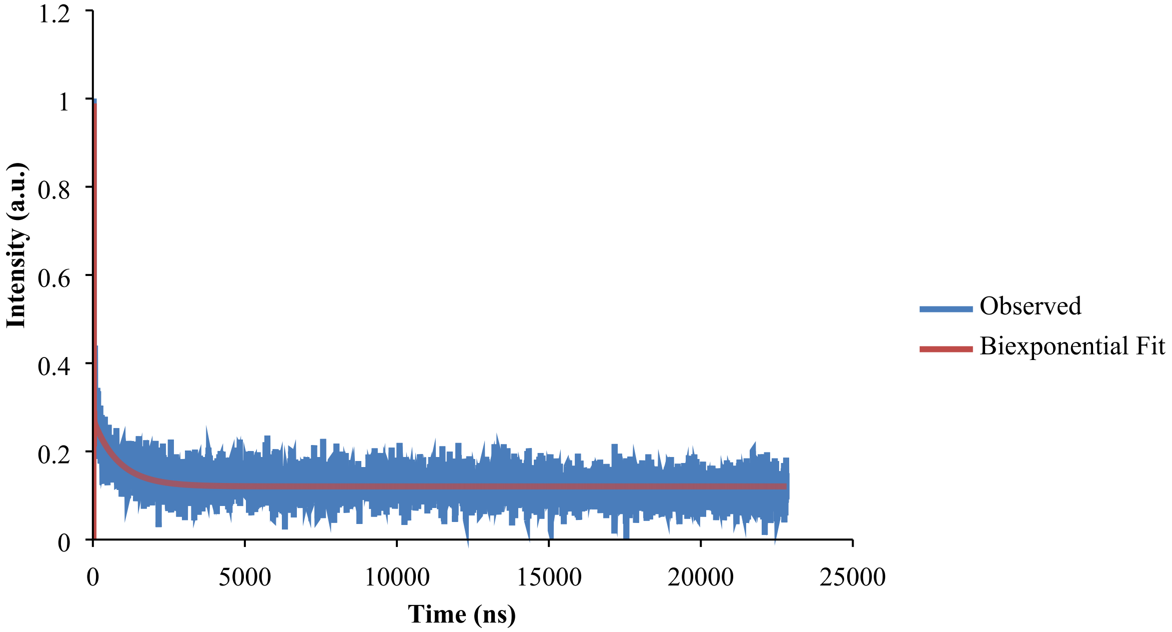


Figure S36. Observed luminescence decay for water treated **1** over 26 μs with a bi-exponential fit.

Table S4. Fitting parameters for the luminescent lifetimes of **1** with different solvent vapour and observation times

Gas	N_2			EtOAc			Water		
Obs. Period	100 ns	26 µs	26 µs	100 ns	26 µs	26 µs	100 ns	26 µs	26 µs
A_1	1.713	0.4927	0.4685	1.777	0.7709	0.4329	-	0.1985	0.9954
A_2	0.1424	-	0.2155	0.2128	-	0.3967	-	-	0.1499
I0	0.08023	0.1845	0.1705	0.1073	0.06283	0.05776	-	0.1214	0.1206
k_1	8.125	0.0006934	0.002474	10.8	0.0005948	0.001114	-	0.00179	0.421
k_2	0.01835	-	0.0002557	0.01544	-	0.0003872	-	-	0.001201
Sigma (ns)	0.0639	0.09962	0.7786	0.06197	0.5191	1.614	-	3.80E-06	0.3709
t0 (ns)	17.96	20.9	20.42	17.93	24.36	23.18	-	19.05	24.76
R^2	0.7798	0.7374	0.6953	0.7629	0.9744	0.9708	-	0.3524	0.2695

$$f_{(y)} = I0 + \frac{(A_1)}{2} e^{\left(k_1{}^2 * \frac{\sigma^2}{2} - ((x - t0) * k_1)\right)} * (1 + \mathrm{erf}\left(\frac{x - t0}{\sigma * \sqrt{2} - \frac{\sigma * k_1}{\sqrt{2}}}\right)) + \frac{(A_2)}{2} e^{\left(k_2{}^2 * \frac{\sigma^2}{2} - ((x - t0) * k_2)\right)} * (1 + \mathrm{erf}\left(\frac{x - t0}{\sigma * \sqrt{2} - \frac{\sigma * k_2}{\sqrt{2}}}\right))$$

Equation S1. Fit for luminescent lifetimes of **1** where I0 is the fitting offset, k_1 and k_2 are the decay rates, A_1 and A_2 are the exponential coefficients, sigma is the width of the excitation pulse and t0 is the time-zero offset. Erf is the error function.

Table S5. Luminescent lifetimes for **1** monitored for various periods under N_2 (as-synthesized), ethyl acetate vapour and water vapour. All lifetimes are in nanoseconds.

Gas	As-synthesized			EtOAc-treated			Water-treated	
Obs. Period	100 ns	26 µs	26 µs	100 ns	26 µs	26 µs	26 µs	26 µs
τ_1 (ns)	0.12	1442.17	404.20	0.09	1681.24	897.67	558.66	2.38
τ_2 (ns)	54.50	-	3910.83	64.77	-	2582.64	-	832.64

NOTE: The EtOAc-treated sample has the highest luminescence intensity, which allows for more reliable lifetime measurement, i.e., R^2 of the fit is 0.97, while the other samples with much weaker intensity, resulting in much lower R^2 of the fit.

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