

Supporting information

“Unraveling of the true MOF-5 luminescence”

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1. Metal-Organic Framework synthesis	3
2. Single crystal X-Ray diffraction	4
3. Powder X-Ray diffraction	5
4. Thermogravimetric analysis (TGA)	5
5. Raman	5
6. N ₂ Adsorption	5
7. Photoluminescence	5
8. Time correlated single photon counting (TCSPC)	5

Figure S1. TGA of activated MOF-5.

Figure S2. Raman spectra of MOF-5 in DMF (black) and without after 68h (red).

Figure S3. Isotherm (top), surface BET plot (middle) and cumulative surface area (bottom) of MOF-5 (black) and partially hydrated MOF-5 (blue)

Figure S4. TCSPC of H₂BDC dissolved in DMSO and MOF-5 impregnated with DMSO showing similar lifetime of 1.5 ns.

Figure S5. TCSPC of H₂BDC dissolved in DMF and MOF-5 impregnated with DMF showing similar lifetime of 1.5 ns

Figure S6. Decay time measurements of hydrated MOF-5 (blue), partially hydrated MOF-5 (red) observed at 350 and 450 nm and MOF-5 soaked in DMF (black).

Figure S7. Perrin-Jablonsky diagram

Figure S8. Decay time measurements of solid H₂BDC (purple), Na₂BDC (red), H₂BDC dilute in DMF (black) and activated MOF-5 (blue).

Figure S9. Surface normalized intensity showing an isobestic point at $\lambda = 410$ nm

Figure S10. Excitation (dashed) and emission (straight) PL spectra of H₂BDC diluted in DMF.

Figure S11. Excitation (dashed) and emission (straight) PL spectra of H₂BDC diluted in DMSO.

Figure S12. Excitation (dashed) and emission (straight) PL spectra of H₂BDC diluted in DCM.

1. Metal-Organic Framework synthesis

Reagents

Zinc nitrate hexahydrate (Alfa Aesar, 99%), benzene-1,4-dicarboxylic acid (Sigma Aldrich, 98%), *N,N*-Diethylformamide (VWR, reagent grade), *N,N*-Dimethylformamide (VWR, reagent grade), Anhydrous *N,N*-Dimethylformamide (VWR, Anhydrous max. 0.005% H₂O), Anhydrous Dichloromethane (VWR, Anhydrous max. 0.005% H₂O) were used as received without further purification.

Synthesis of MOF-5

Zinc nitrate hexahydrate Zn(NO₃)₂•6H₂O (1.77 g, 5.9 mmol) and benzene-1,4-dicarboxylic acid (329 mg, 1.9 mmol) were dissolved in 50 mL of *N,N*-diethylformamide (DEF). The mixture was removed by syringe and injected through a 13 mm syringe filter (0.45 μm PTFE) into ten 20 mL scintillation vials which were then sealed with a screw cap. The vials were placed in an oven at 75 °C for ten days yielding millimeter sized MOF-5 single crystals. The closed vials were removed and placed in a N₂ glovebox.

Activation

1. Classical activation

Single crystals MOF-5 were washed three times with anhydrous DMF. The resulting sample was then washed three times with anhydrous dichloromethane. Activation was realized at 70 °C under reduced pressure and sample were placed in glovebox for further analysis.

2. Supercritical CO₂ activation

Single crystals MOF-5 were washed three times with anhydrous DMF. Activation was realized through supercritical CO₂ using a Tousimis Samdri-PVT-3D and sample were placed in glovebox for further analysis.

2. Single crystal X-Ray diffraction

A translucent colourless parallelepiped-like specimen of $C_{24}H_{12}O_{13}Zn_4$, approximate dimensions 0.124 mm x 0.137 mm x 0.152 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured ($\lambda = 0.71073 \text{ \AA}$).

A total of 939 frames were collected. The total exposure time was 2.61 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm.

Table 1. Single crystal data

Chemical formula	$C_{24}H_{12}O_{13}Zn_4$	
Formula weight	769.82 g/mol	
Temperature	220(2) K	
Wavelength	0.71073 \AA	
Crystal size	0.124 x 0.137 x 0.152 mm	
Crystal habit	translucent colourless parallelepiped	
Crystal system	cubic	
Space group	Fm $\bar{3}$ m	
Unit cell dimensions	a = 25.8107(9) \AA b = 25.8107(9) \AA c = 25.8107(9) \AA	$\alpha = 90^\circ$ $\beta = 90^\circ$ $\gamma = 90^\circ$
Volume	17194.9(18) \AA^3	
Z	8	
Density (calculated)	0.595 g/cm ³	
Absorption coefficient	1.123 mm ⁻¹	
F(000)	3040	
Theta range for data collection	2.23 to 25.63°	
Index ranges	-29 ≤ h ≤ 31, -31 ≤ k ≤ 31, -31 ≤ l ≤ 31	
Reflections collected	64578	
Independent reflections	878 [R(int) = 0.1669]	
Coverage of independent reflections	99.7%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.7471 and 0.6052	
Structure solution technique	direct methods	
Structure solution program	SHELXT 2014/5 (Sheldrick, 2014)	
Refinement method	Full-matrix least-squares on F ²	
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)	
Function minimized	$\sum w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	878 / 0 / 25	
Goodness-of-fit on F²	1.119	
Final R indices	596 data; $I > 2\sigma(I)$	R1 = 0.0619, wR2 = 0.1692
	all data	R1 = 0.0883, wR2 = 0.1831
Weighting scheme	$w = 1 / [\sigma^2(F_o^2) + (0.1021P)^2 + 46.1761P]$ where $P = (F_o^2 + 2F_c^2) / 3$	
Largest diff. peak and hole	0.556 and -0.338 e \AA^{-3}	
R.M.S. deviation from mean	0.067 e \AA^{-3}	

3. Powder X-Ray diffraction

Single crystalline samples were gently crushed on a sample holder.

PXRD data was collected on a Bragg Brentano diffractometer (Siemens D5000) equipped with Cu K α X-Ray source operating at 40 kV and 40 mA. Diffraction data was collected in a θ -2 θ geometry through a 2 θ range of 3°-50° with step size of 0.03° and a 5 s acquisition.

4. Thermogravimetric analysis (TGA)

Approximately 5 – 10 mg sample was used for thermogravimetric analysis. The sample was analyzed under a stream of argon using a Perkin Elmer TGA4000 from room temperature up to 600 °C with a scan rate of 1 °C.min⁻¹.

5. Raman

Raman spectra were collected at room temperature, using a WiTec alpha 300R confocal Raman microscope with a UHTS300 spectrometer and a DV401A CCD detector. The laser beam spot size was around 900nm. MOF-5 and MOF-5 t+68h were illuminated using a frequency doubled Nd:YAG Laser at 532 nm and Raman signal was collected in a backscattering geometry.

6. N₂ Adsorption

MOFs were degassed under vacuum for 3 hours at 100°C. Adsorption–desorption isotherms were then recorded at 77 K with a Micrometrics ASAP 2010 volumetric analyser using N₂ as adsorptive. The surface area and pore diameter were deduced from these measurements using the Brunauer–Emmet–Teller (BET) and micropore analysis (MP) methods. Micropore area was determined by the t-plot method

7. Photoluminescence

Dilute solution of H₂BDC were prepared and filled in supra quartz cuvette. MOF-5 single crystal was placed in quartz capillary in N₂ glovebox and excess solvent wicked. Capillary was then sealed to avoid any moisture degradation. Activated MOF-5, Na₂BDC and H₂BDC were squeezed between two quartz slides into the glovebox.

PL data was collected on a Horiba Jobin-Yvon FluoroLog-3 fluorescence spectrometer at the right angle and appropriate filter to avoid lamp diffusion. Slit widths of 3 nm (excitation) and 3 nm (emission) were used for dilute solution of H₂BDC. Larger slit widths of 4 nm and 4 nm, and smaller slits widths of 1.5 nm and 1.5 nm were used for single crystal and powder samples, respectively. Acquisition was fixed at 1 s to increase the SNR (Signal to Noise Ratio). PL data for moisture degradation was collected at the right angle between 330 and 550 nm with 110 s delay between each measurement.

8. Time correlated single photon counting (TCSPC)

Samples for TCSPC were prepared as previously described for PL measurements.

Fluorescent lifetimes are obtained using TCSPC method. Excitation is made by a femtosecond TiSa laser pumped by a Nd:YVO₄ laser. The repetition rate can be tuned up to 4 MHz. Harmonic generator permits to assess a 300 nm excitation. Pulses were focused on the sample at the appropriate angle and collected by a monochromator at the desired wavelength. Filtered emission was detected with a microchannel plate photomultiplier tube (R3809U-50, Hamamatsu) connected to TCSPC board (SPC 630, Becker & Hickl). Data were normalized with instrumental response subtracted and fit using mono or biexponential decay.

$$EQ(1) : y = y_0 + a_1 e^{-(x-x_0)/\tau_1} + a_2 e^{-(x-x_0)/\tau_2}$$

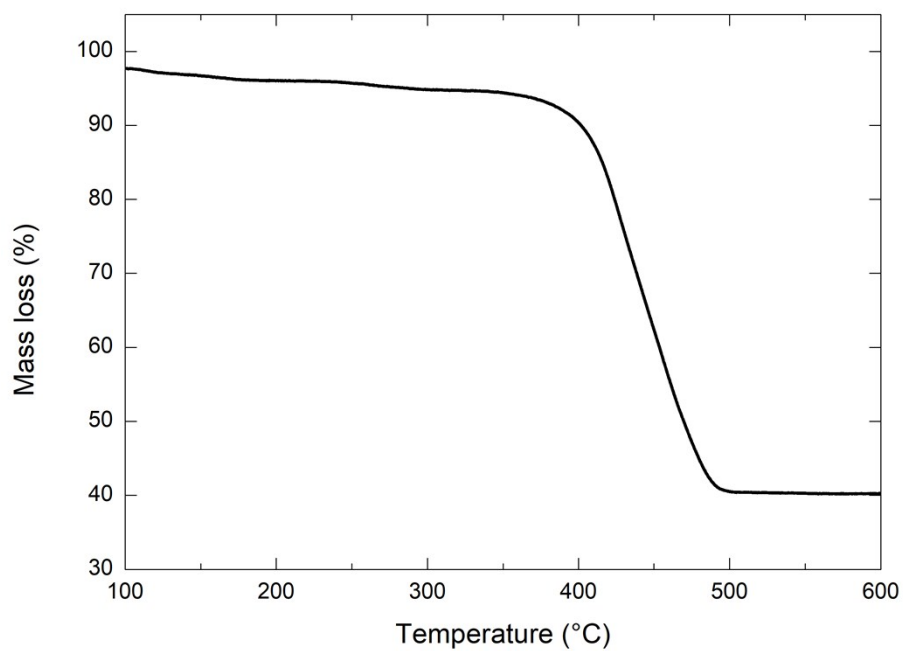


Figure S1. TGA of activated MOF-5.

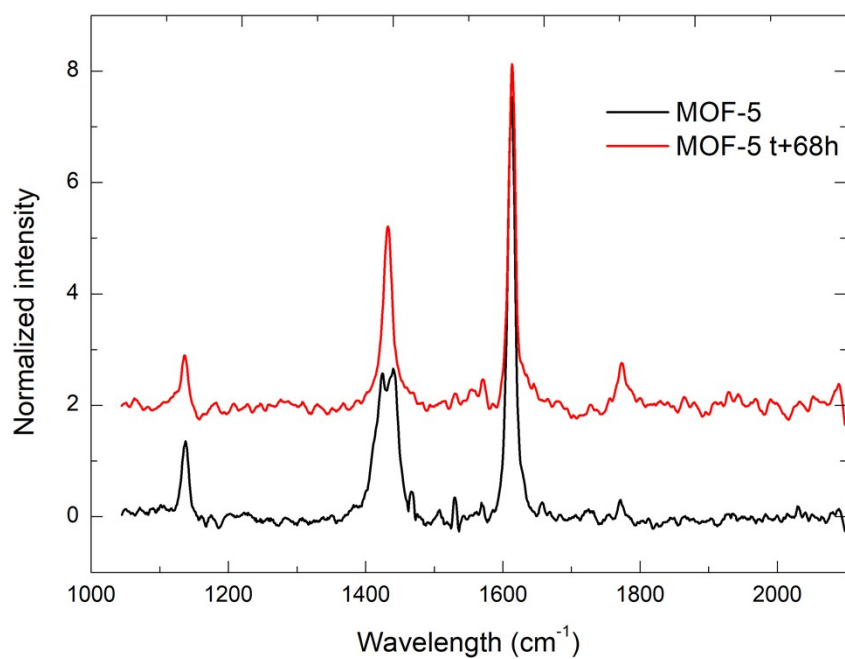


Figure S2. Raman spectra of MOF-5 in DMF (black) and without after 68h (red).

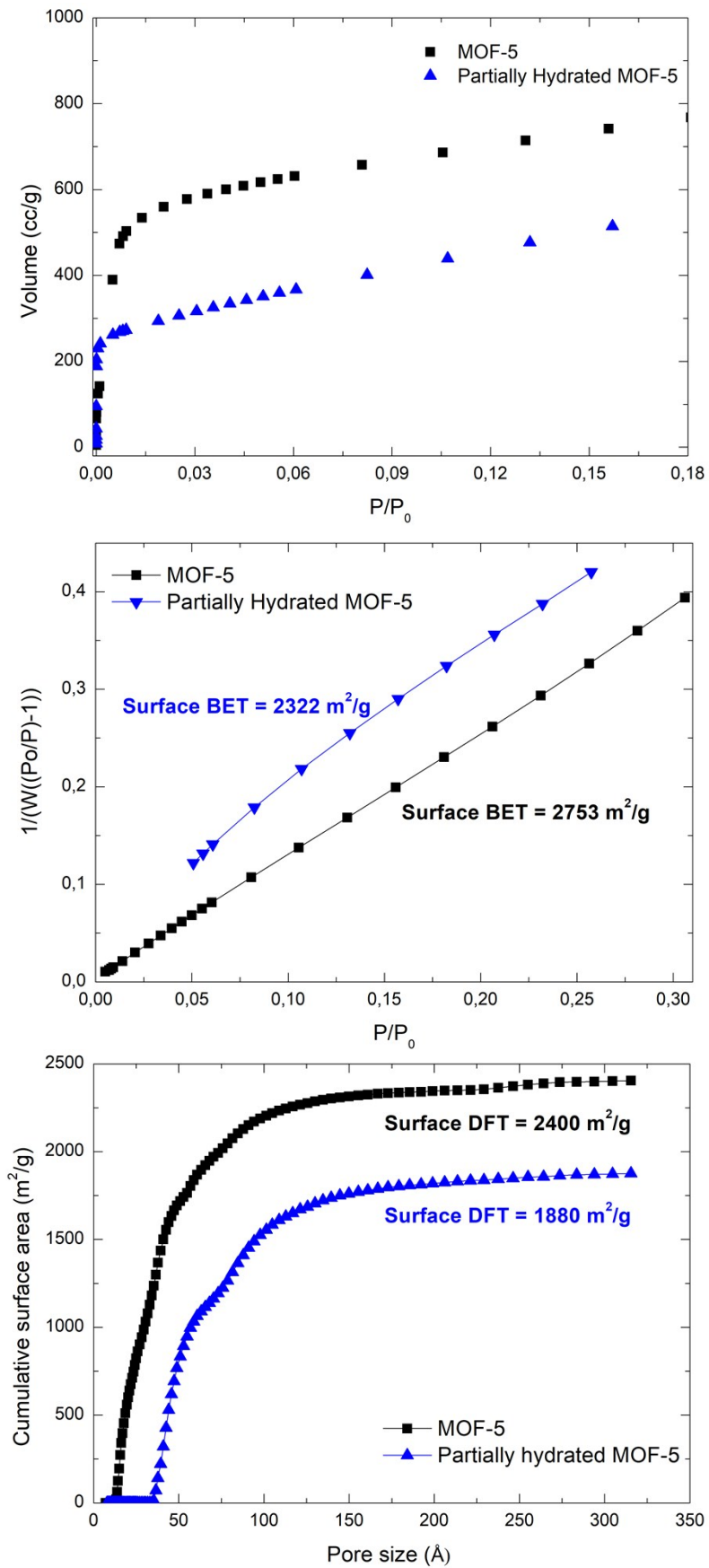


Figure S3. Isotherm (top), surface BET plot (middle) and cumulative surface area (bottom) of MOF-5 (black) and partially hydrated MOF-5 (blue)

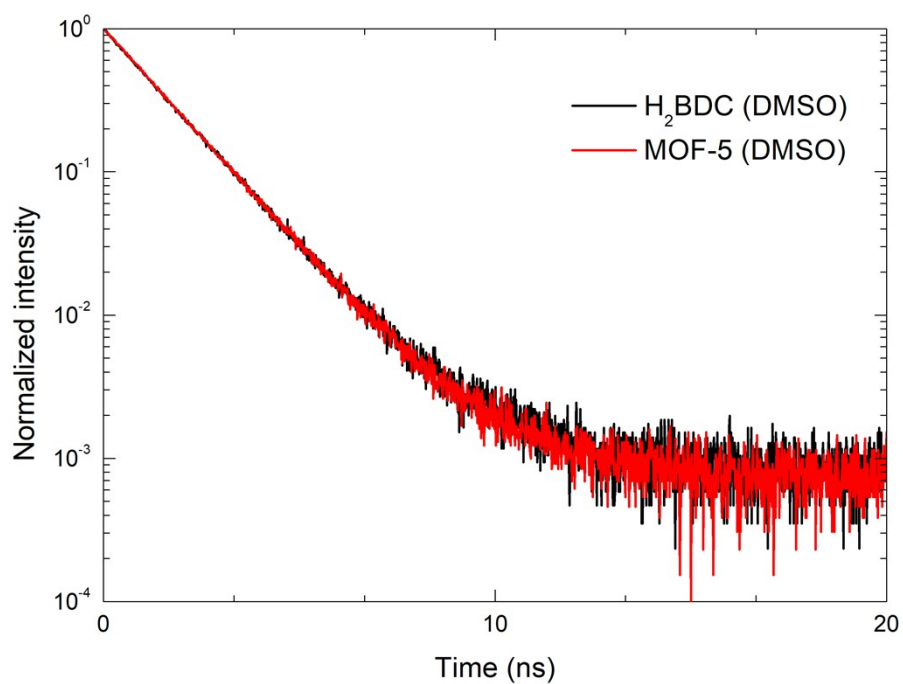


Figure S4. TCSPC of H₂BDC dissolved in DMSO and MOF-5 impregnated with DMSO showing similar lifetime of 1.5 ns.

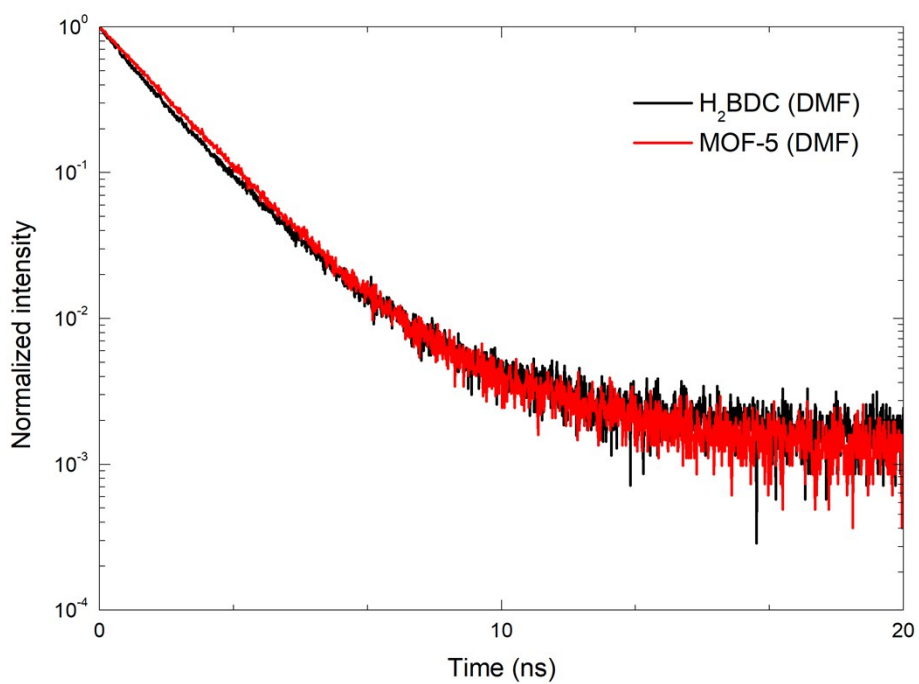


Figure S5. TCSPC of H₂BDC dissolved in DMF and MOF-5 impregnated with DMF showing similar lifetime of 1.5 ns.

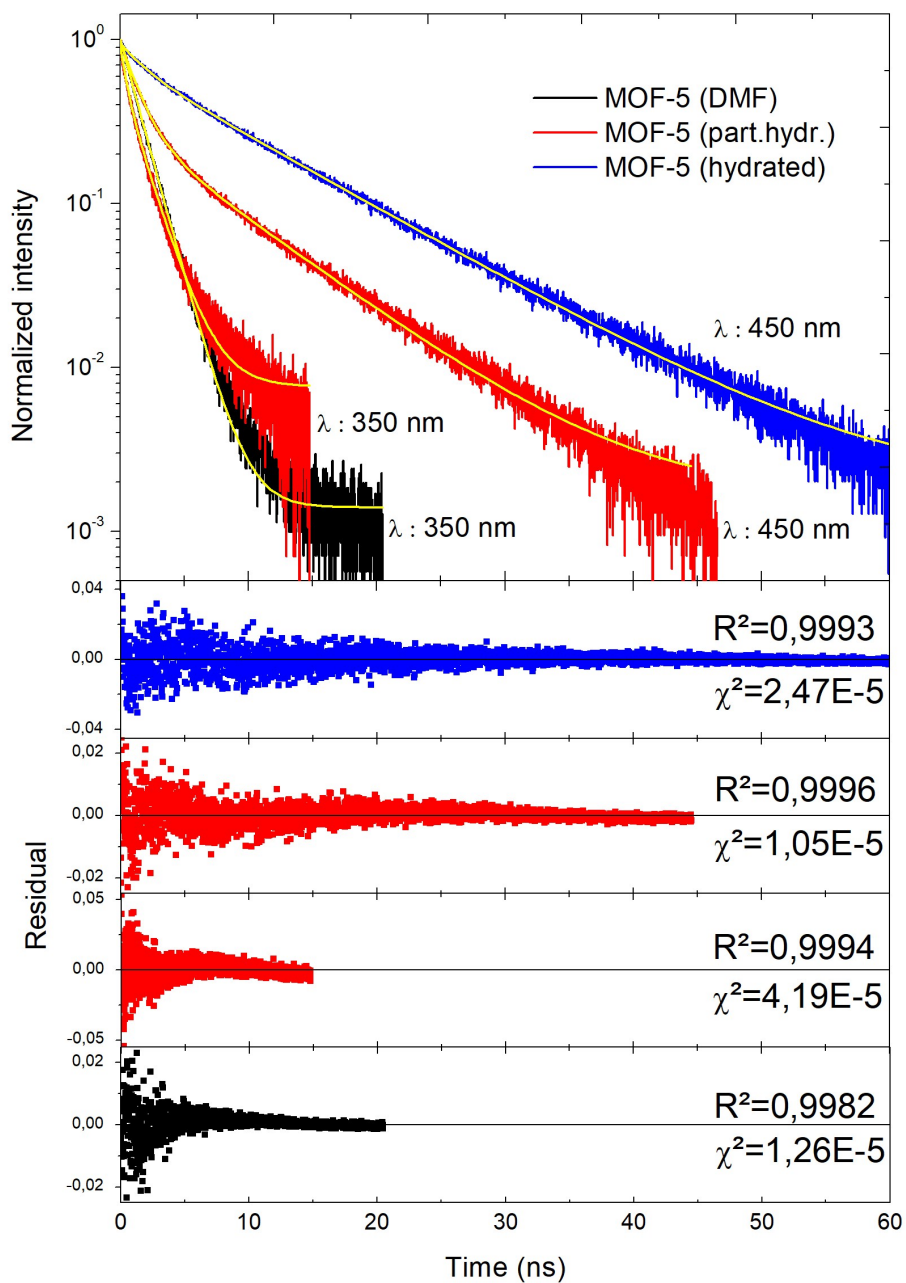


Figure S6. Decay time measurements of hydrated MOF-5 (blue), partially hydrated MOF-5 (red) observed at 350 and 450 nm and MOF-5 soaked in DMF (black).

	MOF-5 (DMF)	MOF-5 (part. hydr.)		MOF-5 (hydrated)
τ_1 (ns)	1.5±0.1	1.5±0.1	1.4±0.1 (77%)	1.8±0.1 (25%)
τ_2 (ns)	-	-	8.6±0.1 (23%)	9.8±0.1 (75%)

Table 2. Associated lifetimes

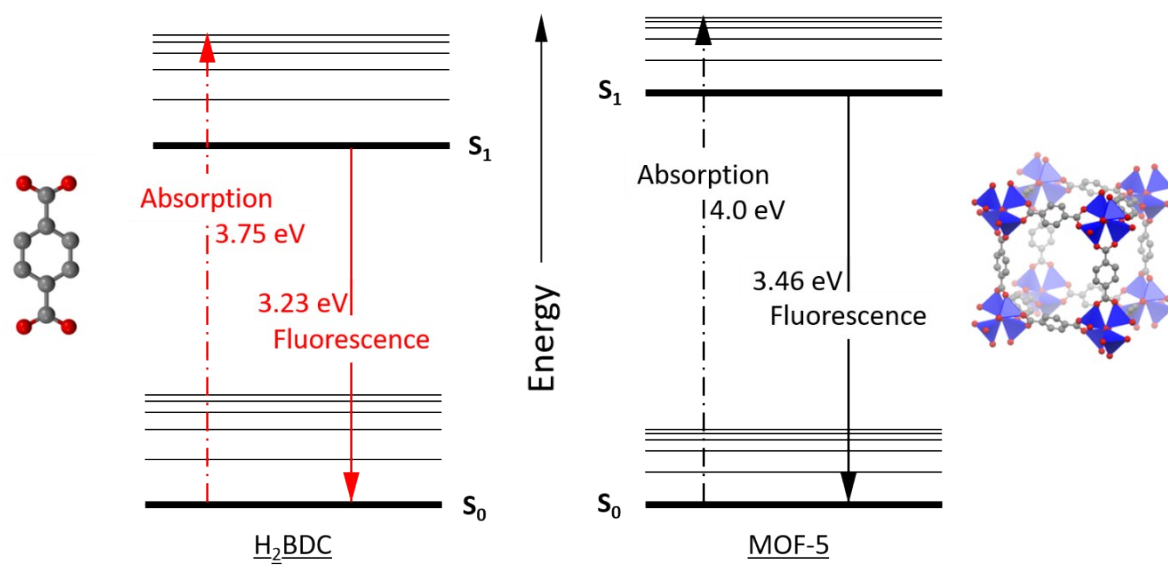


Figure S7. Perrin-Jablonsky diagram

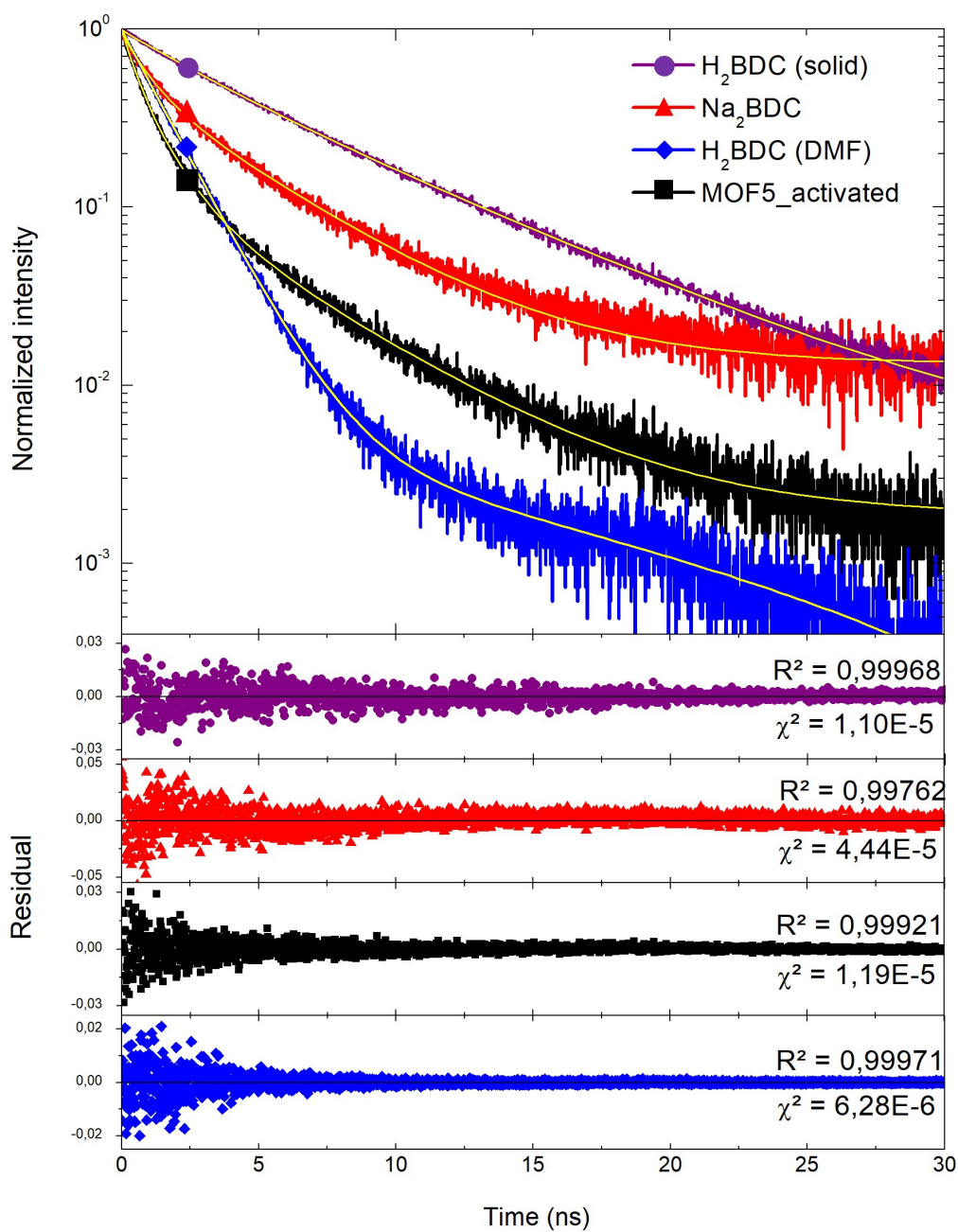


Figure S8. Decay time measurements of solid H₂BDC (purple), Na₂BDC (red), H₂BDC dilute in DMF (black) and activated MOF-5 (blue).

	H_2BDC (solid)	Na_2BDC	H_2BDC (DMF)	Activated MOF-5
τ_1 (ns)	3.0 ± 0.1 (35%)	1.3 ± 0.1 (50%)	1.5 ± 0.1	1.4 ± 0.1 (77%)
τ_2 (ns)	6.7 ± 0.1 (65%)	4 ± 0.1 (50%)	-	4.5 ± 0.1 (23%)

Table 3. Associated lifetimes

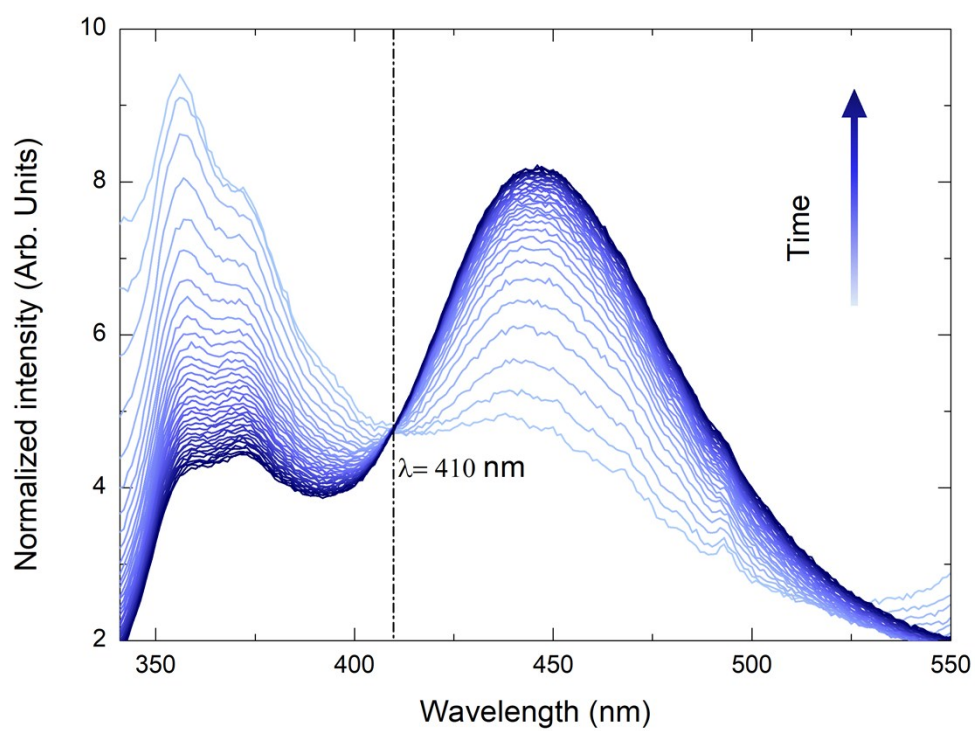


Figure S9. Surface normalized intensity showing an isobestic point at $\lambda = 410 \text{ nm}$

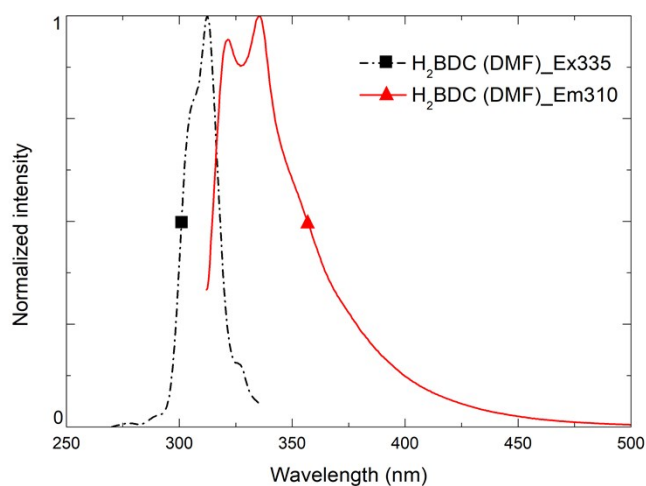


Figure S10. Excitation (dashed) and emission (straight) PL spectra of H2BDC diluted in DMF.

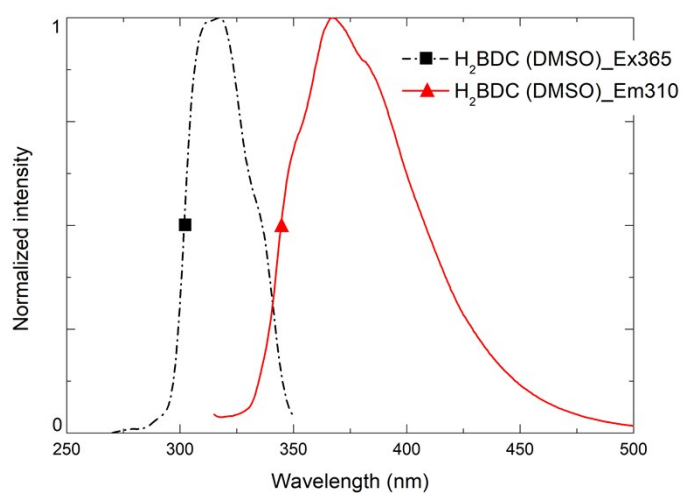


Figure S11. Excitation (dashed) and emission (straight) PL spectra of H2BDC diluted in DMSO.

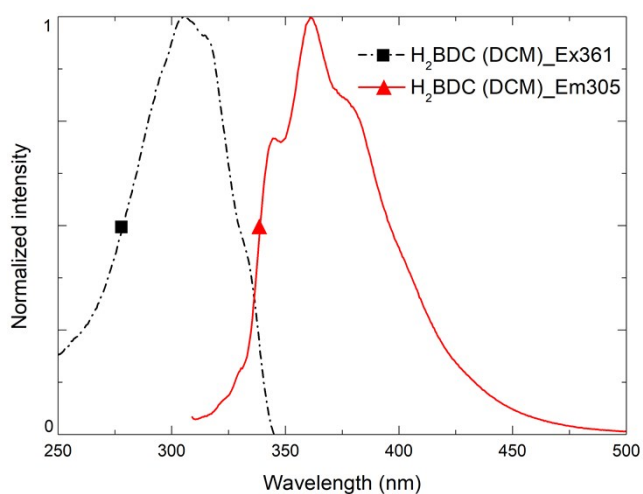


Figure S12. Excitation (dashed) and emission (straight) PL spectra of H2BDC diluted in DCM.