Supporting Information

Luminescent properties of mixed-ligand MOFs containing fluorene scaffolds functionalized with isonicotinoyl arms

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Content

^{1}H NMR analysis

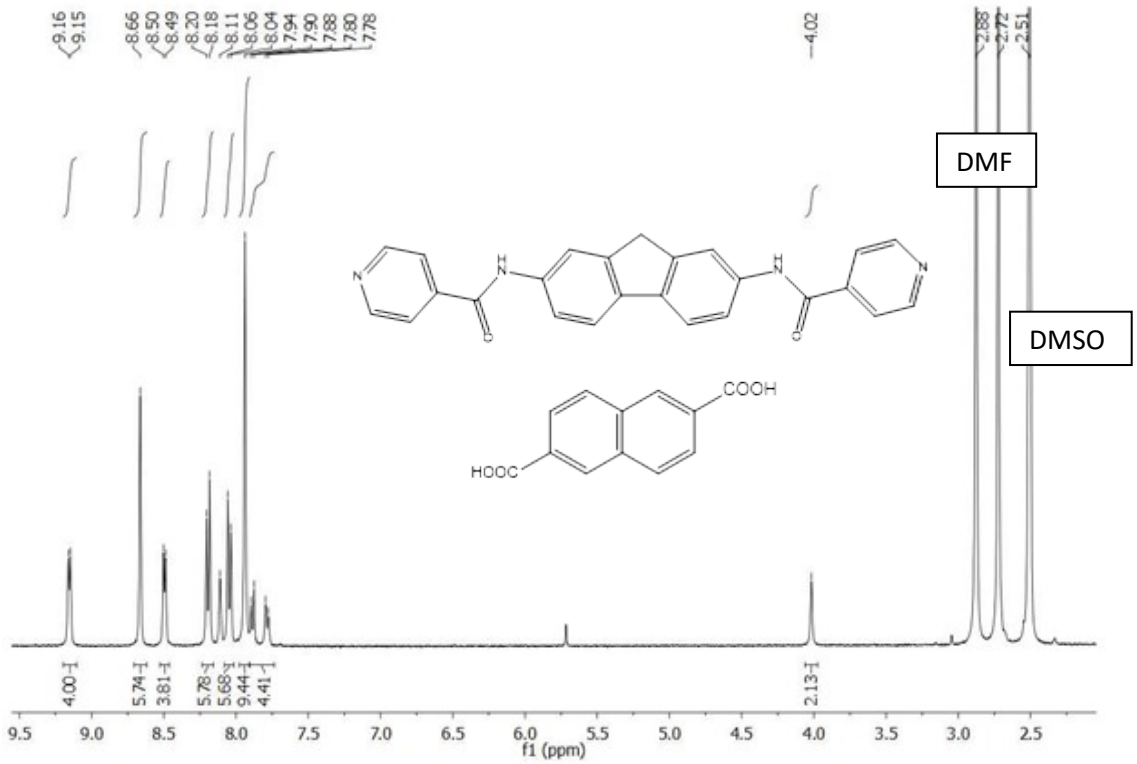

Figure S1 ^{1}H NMR spectrum of **PUM310** crystals after digestion in TFA-d. Spectrum recorded at 25°C after dilution with DMSO-d.

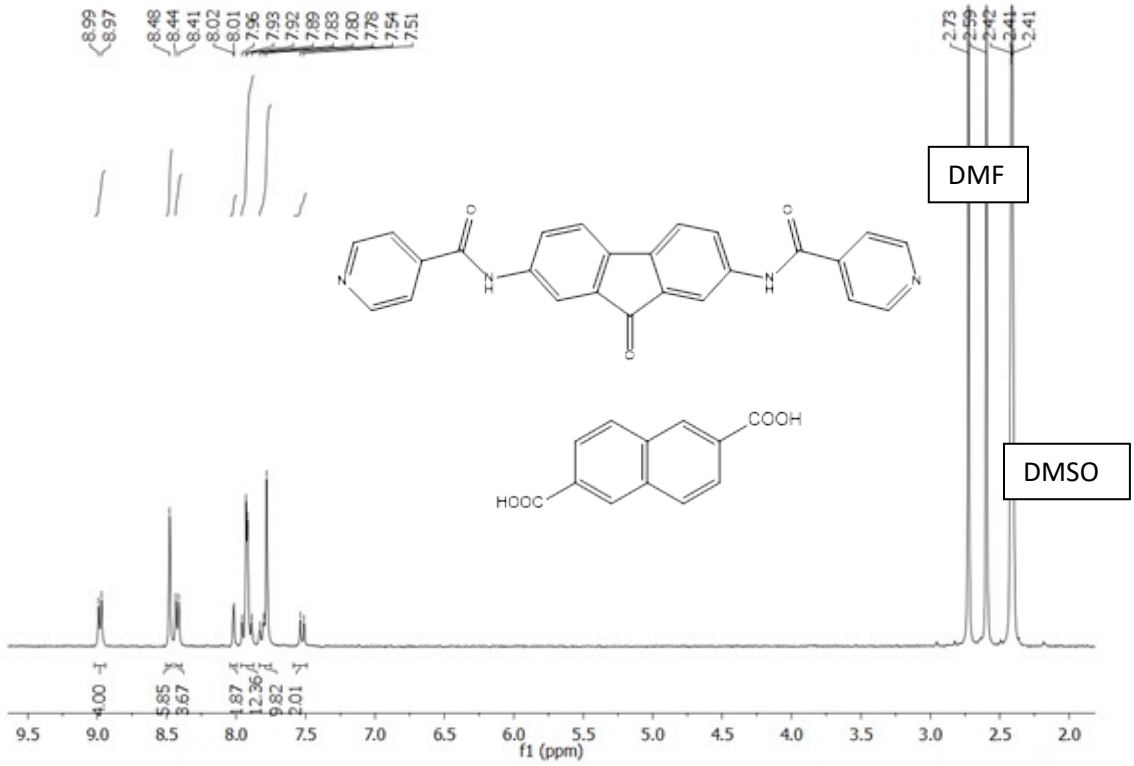

Figure S2 ^{1}H NMR spectrum of **PUM310CO** crystals after digestion in TFA-d. Spectrum recorded at 25°C after dilution with DMSO-d.

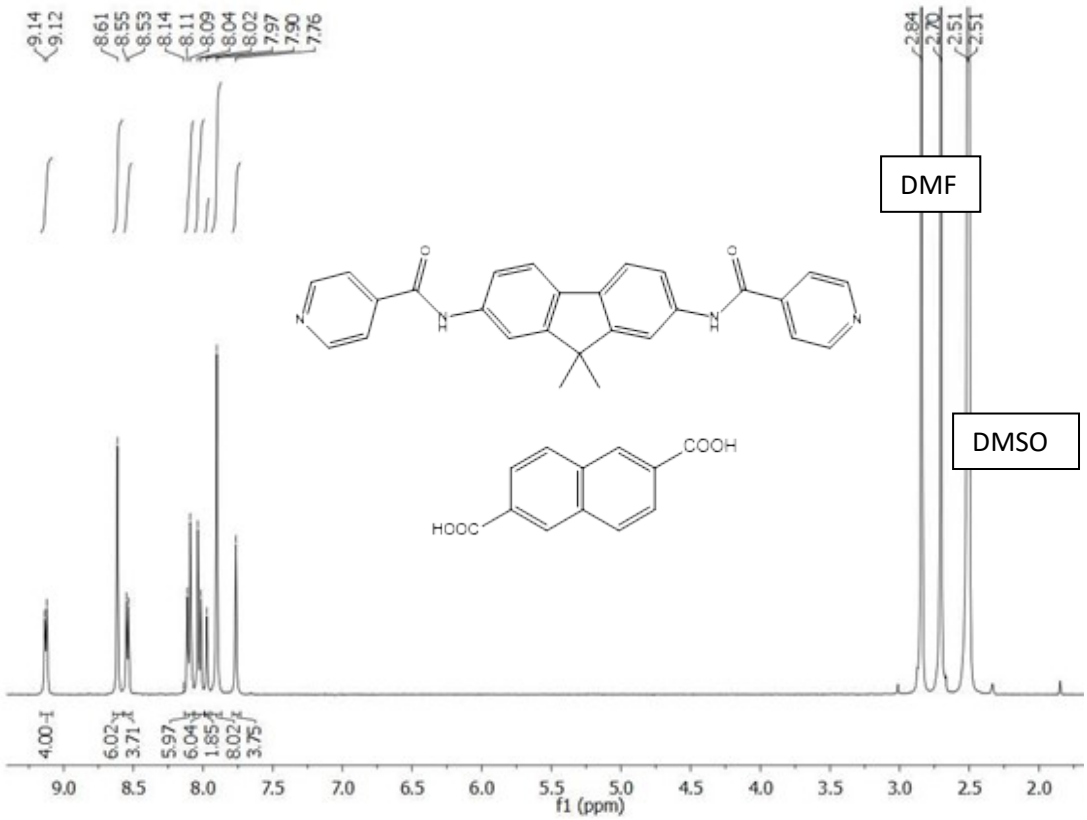

Figure S3 ^{1}H NMR spectrum of **PUM310Me$_2$** crystals after digestion in TFA-d. Spectrum recorded at 25°C after dilution with DMSO-d.

TGA analyses

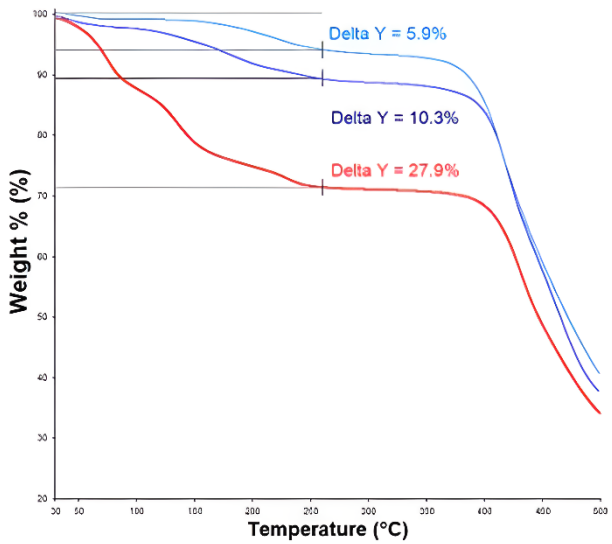

Figure S4 TGA trace of **PUM310** (red), **PUM310-a** (blue) and **PUM310-a'** (light blue).

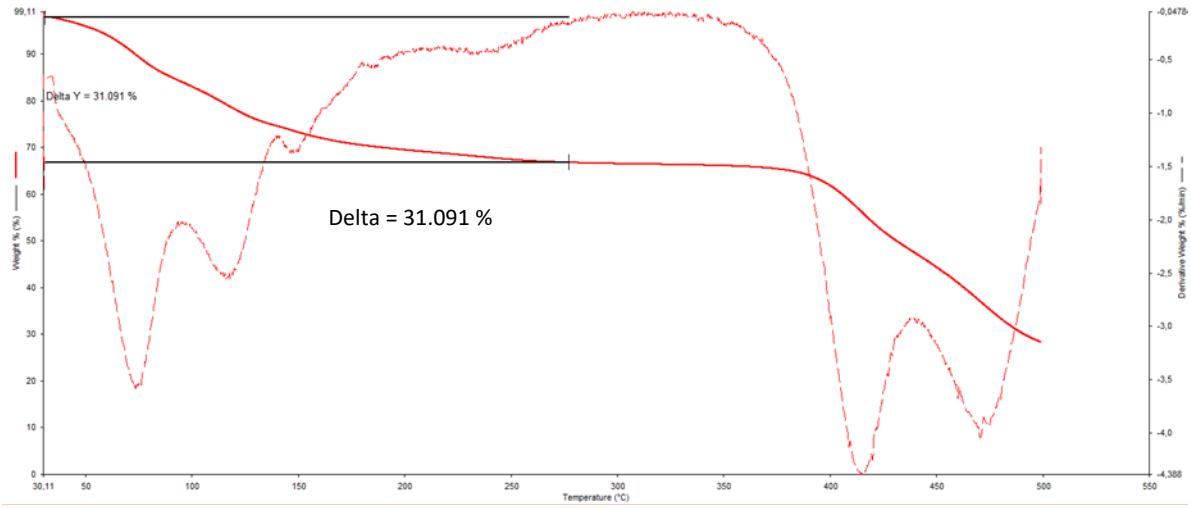

Figure S5 TGA trace of **PUM310CO.**

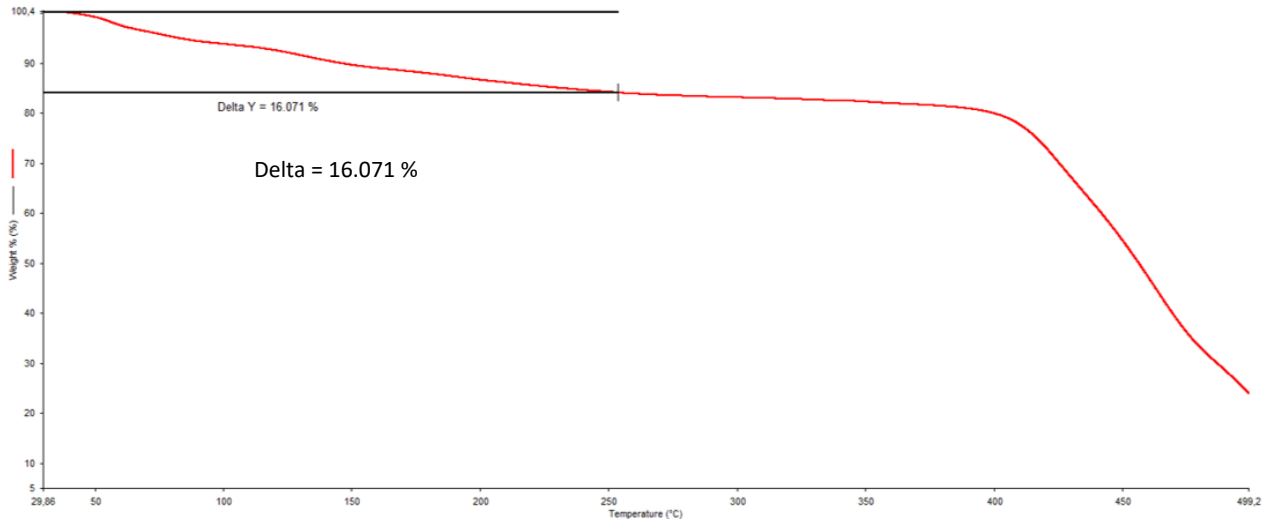

Figure S6 TGA trace of **PUM310Me$_2$.**

Crystallography

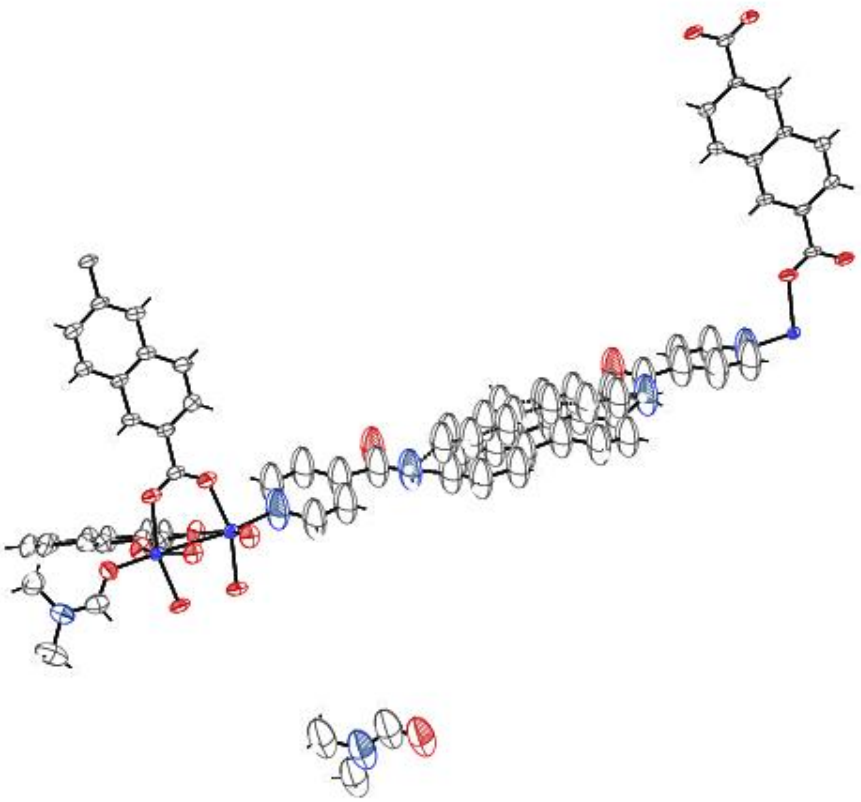

Figure S7 Ortep drawing of the ASU of **PUM310** All non-hydrogen atoms are shown as ellipsoids at the 50% probability level. H atoms (isotropically refined) are reported in capped-stick style for the sake of clarity. Colour code: red=O, blue=N, white=C.

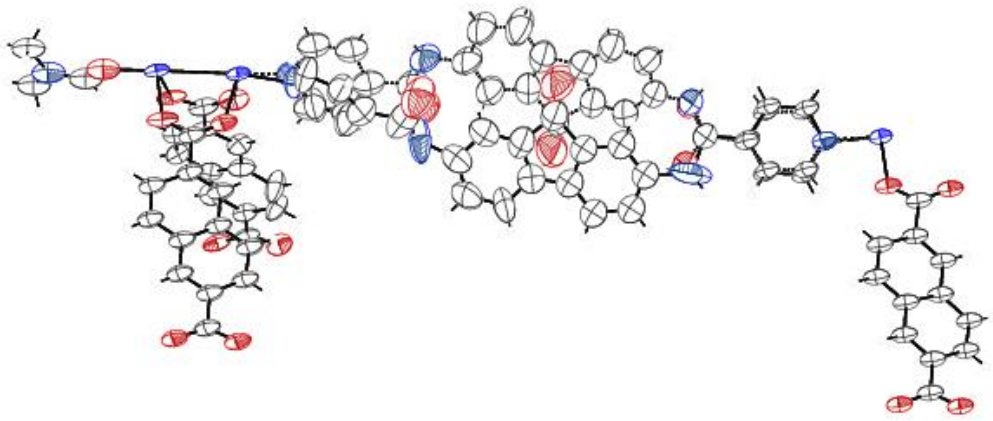

Figure S8 Ortep drawing of the ASU of **PUM310CO**. All non-hydrogen atoms are shown as ellipsoids at the 50% probability level. H atoms (isotropically refined) are reported in capped-stick style for the sake of clarity. Colour code: red=O, blue=N, white=C. Disordered ligand is reported for completeness.

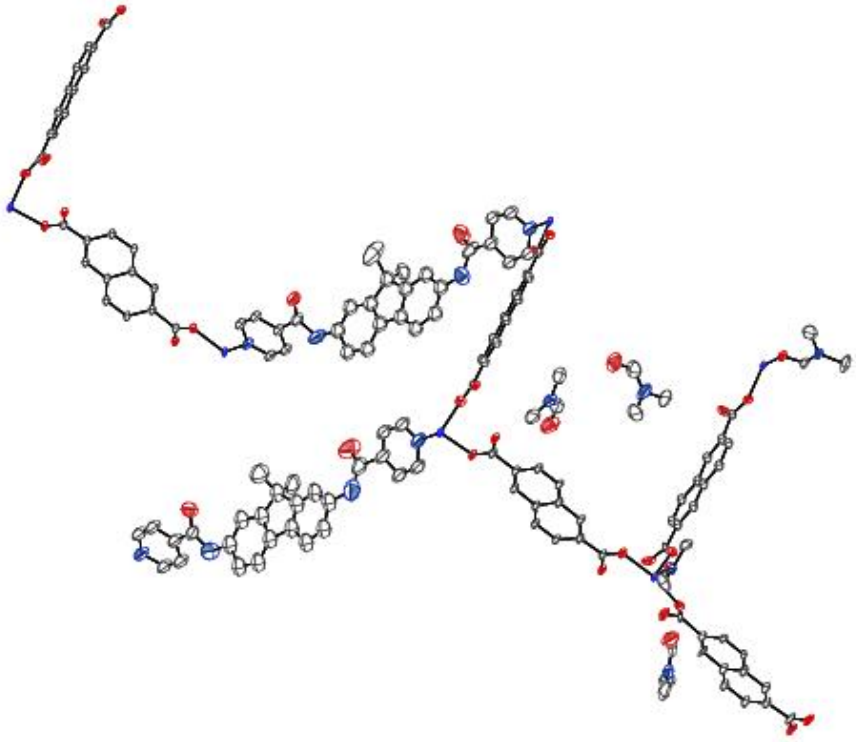

Figure S9 Ortep drawing of the ASU of **PUM310Me$_2$**. All non-hydrogen atoms are shown as ellipsoids at the 50% probability level. H atoms (isotropically refined) are reported in capped-stick style for the sake of clarity. Colour code: red=O, blue=N, white=C.

Topological analysis

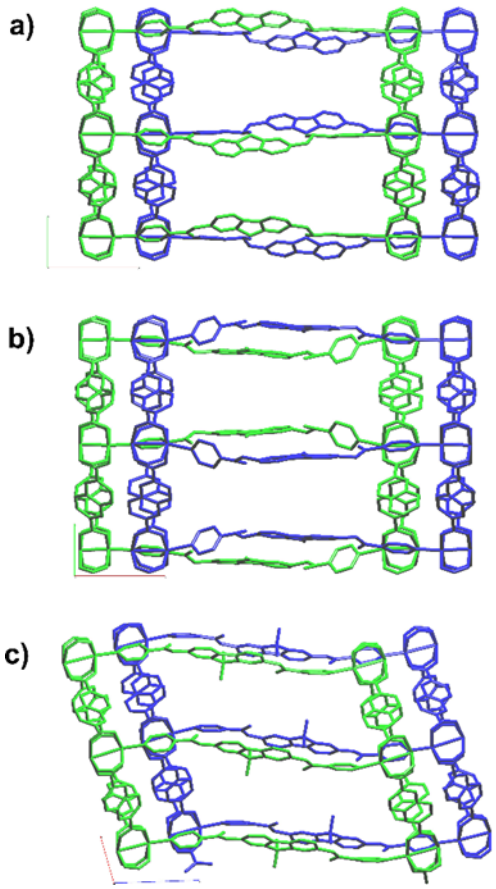

Figure S10 Molecular views of two catenated cubic cages of the thick layers in (a) **PUM310,** (b) **PUM310CO** and (c) **PUM310Me$_2$** showing the arrangement of the ligands in the three structures.

MOF activation-XRPD analysis

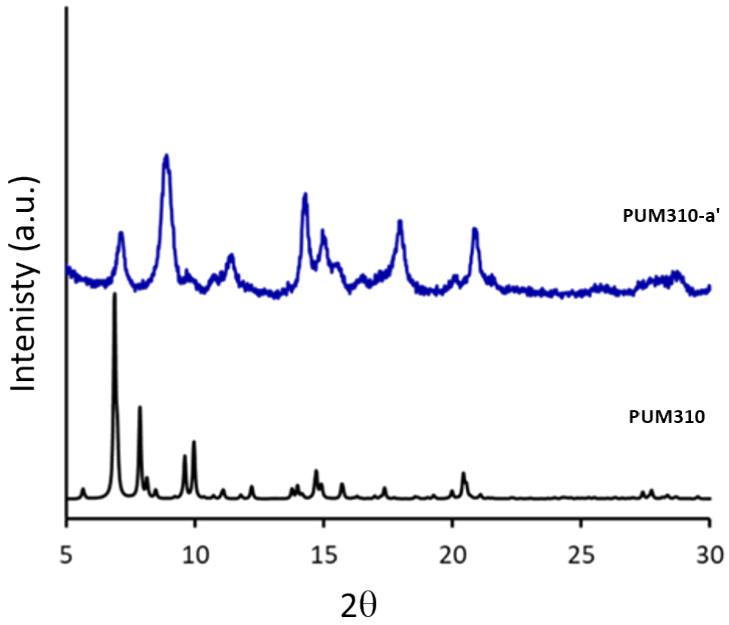

Figure S11 Comparison between the calculated XRPD trace of **PUM310** (black) and **PUM310-a'** (blue).

Volumetric adsorption properties

PUM310, **PUM310CO** and **PUM310Me$_2$** were subjected to N_2 and CO_2 adsorption isotherm analyses.

N_2 adsorption isotherms at 77 K and CO_2 adsorption isotherms at 195 K were collected up to 1 bar using Micromeritics analyser ASAP2020 HD. **PUM310Me$_2$** was previously activated at 70°C under dynamic vacuum for 5 hours, then overnight under dynamic vacuum before the collection of N_2 and CO_2 isotherms. **PUM310** underwent a thermal treatment at 70°C under dynamic vacuum for 2h, then at 60°C for 30 min and outgassing overnight under dynamic vacuum before gas adsorption measurements.

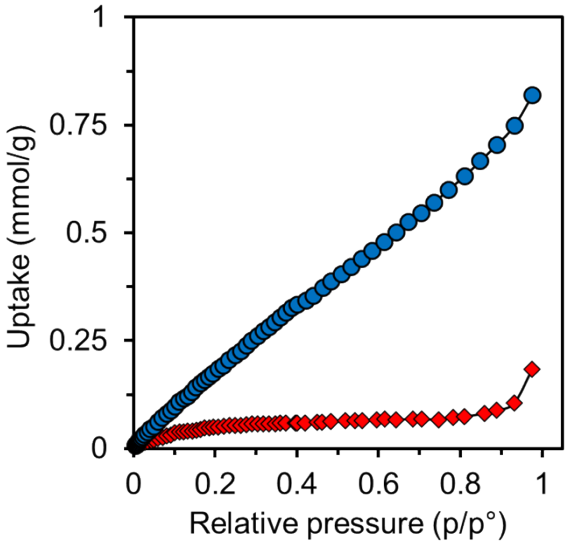

Figure S12 N_2 adsorption isotherms, collected at 77 K, of **PUM310** (red diamonds) and **PUM310Me2** (blue circles).

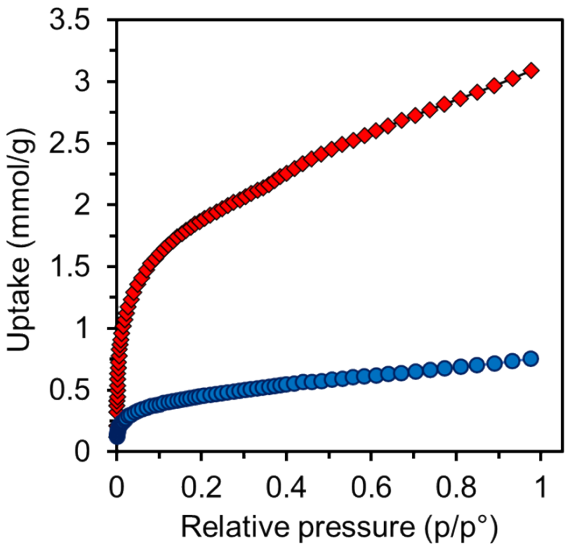

Figure S13 CO_2 adsorption isotherms, collected at 195 K, of **PUM310** (red diamonds) and **PUM310Me$_2$** (blue circles).

Sample	CO_2 adsorption at 0.98 p/p° (mmol/g)
PUM310	3.09
PUM310Me$_2$	0.76

For **PUM310CO** no significative results were obtained.

Luminescence and UV-vis characterization

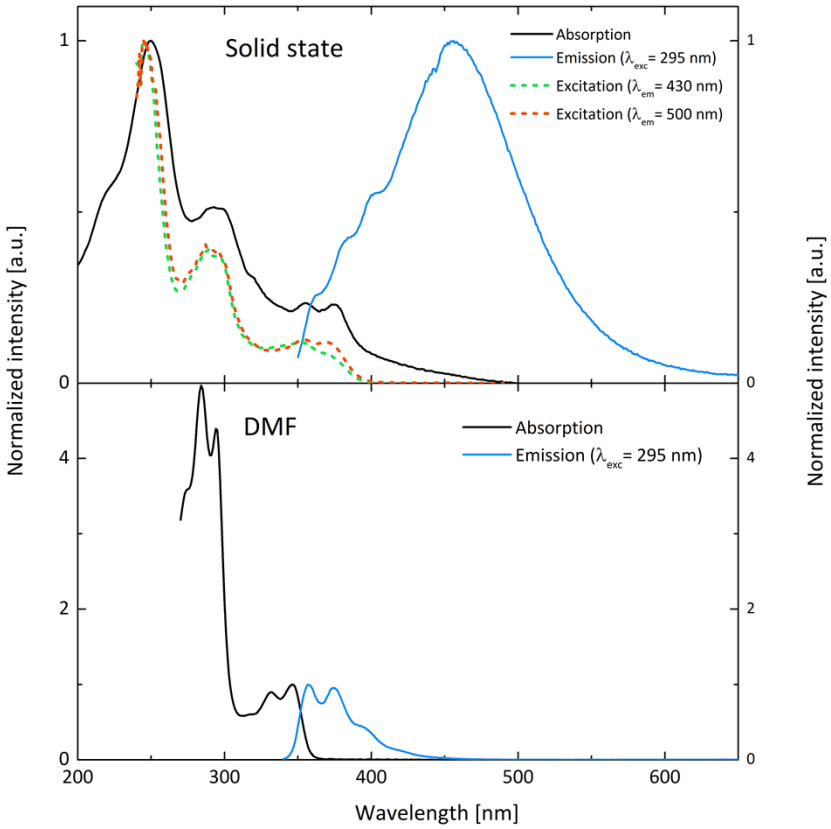

Figure S14 Top: solid state absorption, fluorescence emission and excitation spectra of H_2ndca. Bottom: absorption and emission spectra of H_2ndca in DMF. The corresponding excitation and emission wavelengths are reported in the legend.

The emission spectrum recorded on a thin film of ground powders of H_2ndca is characterized by a broad emission band peaked at 450 nm, which is absent in the spectrum of H_2ndca in solution, and could be due to the formation of excimer species. In the solid-state emission spectrum, a reminder of the emission band of H_2ndca in solution is observed, recognizable thanks to the vibronic peaks (350-400 nm spectral region).

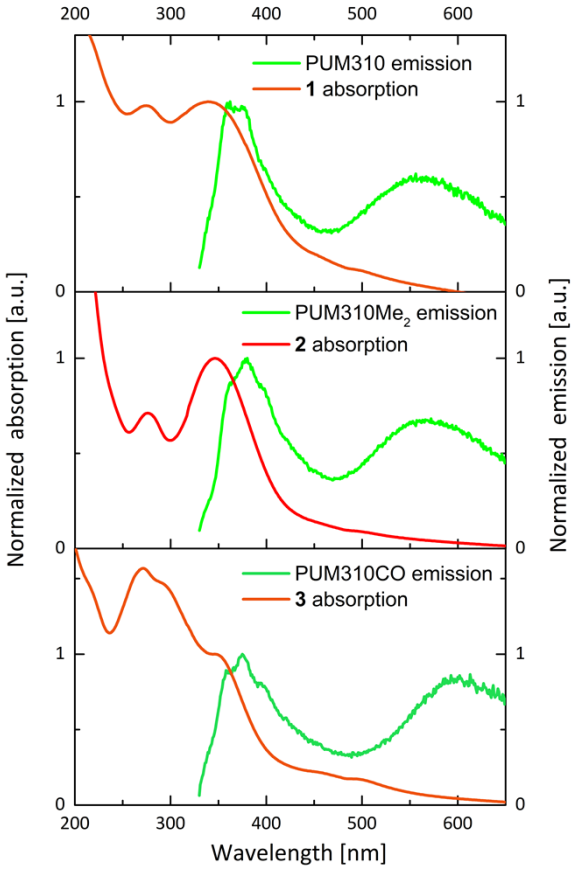

Figure S15 Comparison between solid state absorption of **1**, **2**, **3** (from top to bottom) and emission of H_2ndca when incorporated in the corresponding MOFs structure.