Electronic Supplementary Material (ESI) for Molecular Systems Design & Engineering.

Supporting Information

Specific Recognition of Toxic Allyl Alcohol by Pore-Functionalized Metal-Organic Frameworks

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Figures:

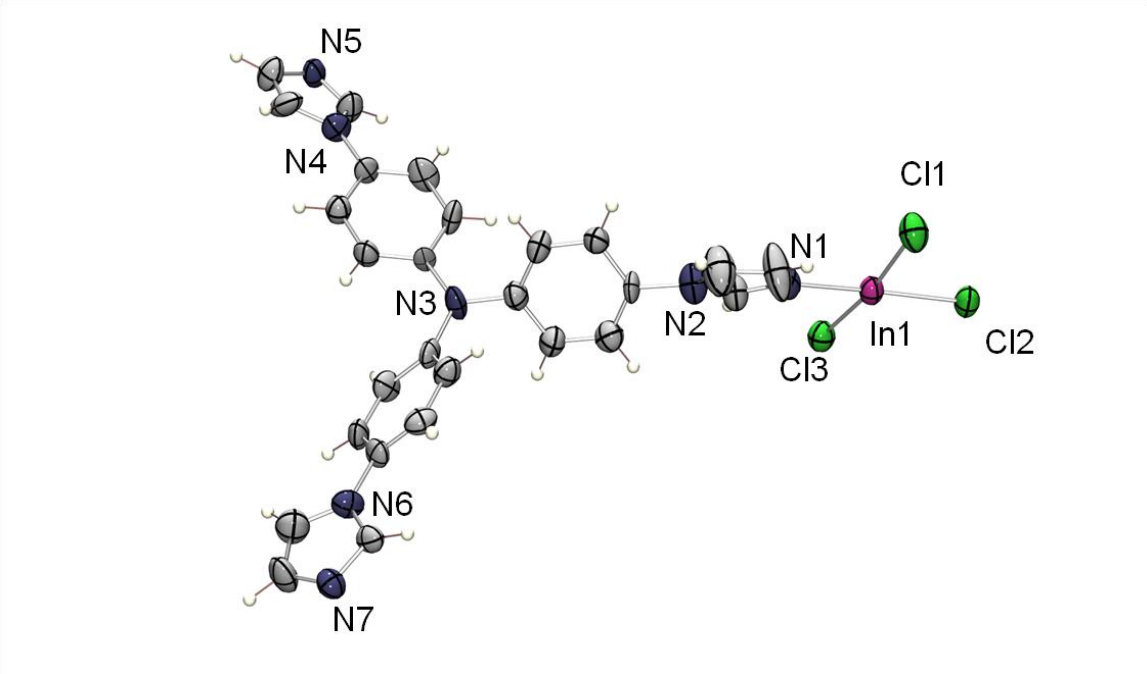

Figure S1: ORTEP diagram for **IPM-303** in thermal ellipsoids.

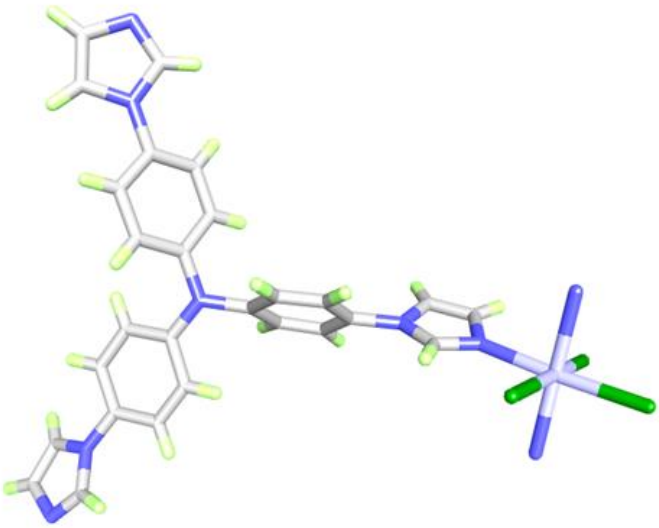

Figure S2: Coordination environment of **IPM-303**. (Colour code: C, grey; N, blue; In, pale violet; Cl, green; H, pale green).

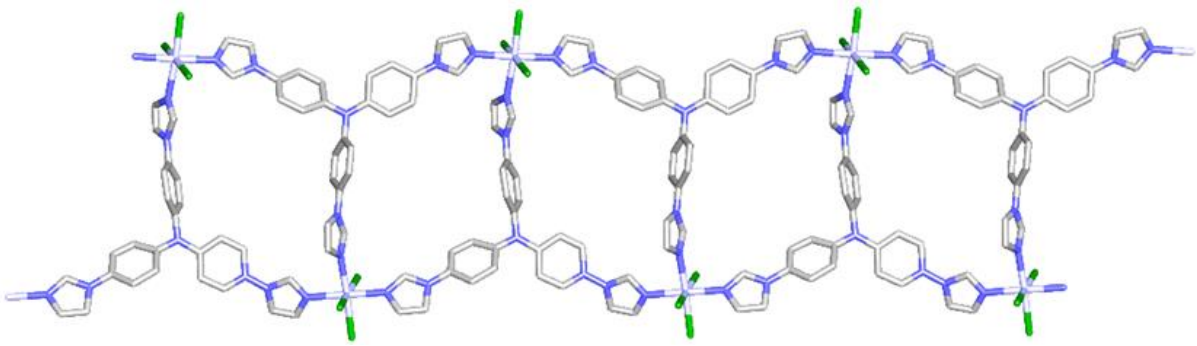

Figure S3: Packing in **IPM-303** showing 1D extension of coordination polymer. (Hydrogen atoms have been omitted for clarity, colour: Gray - C, Blue - N, Light purple - In, Green - Cl).

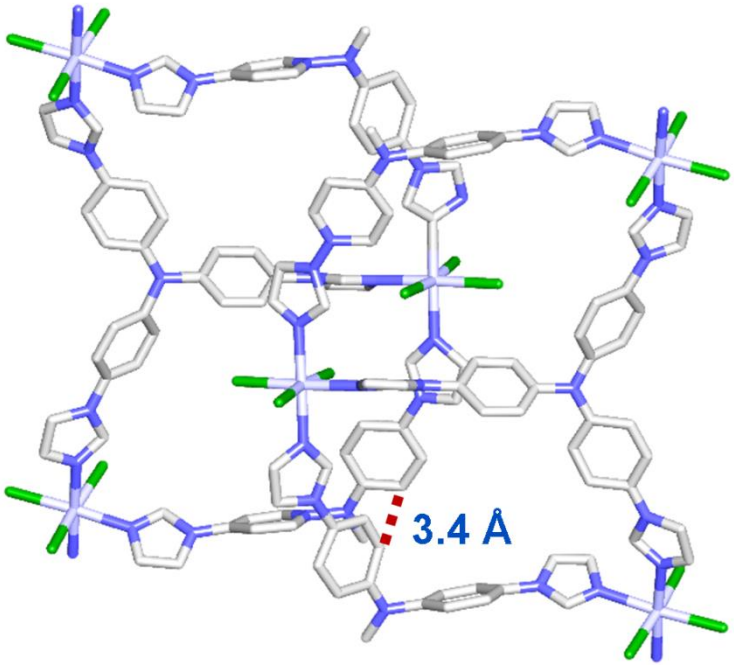

Figure S4: Packing diagram of **IPM-303** showing interaction between adjacent 1D layers. (Hydrogen atoms have been omitted for clarity, colour: Gray - C, Blue - N, Light purple - In, Green - Cl).

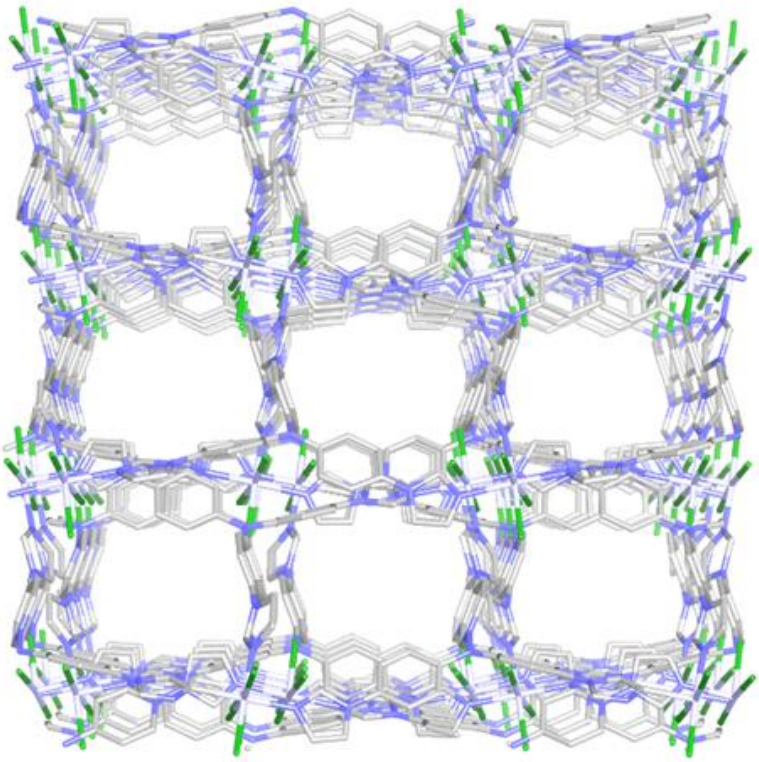

Figure S5: Packing diagram of **IPM-303** showing porous channel. (Hydrogen atoms have been omitted for clarity, colour: Gray - C, Blue - N, Light purple - In, Green - Cl).

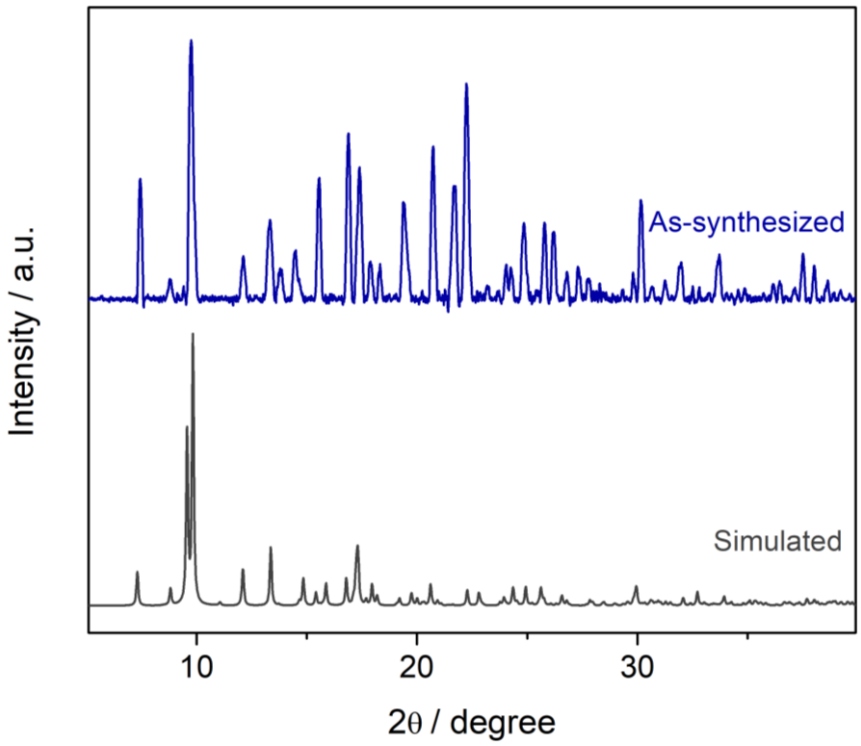

Figure S6: Powder X-ray diffraction patterns of **IPM-303** - Simulated (gray), as-synthesized (blue).

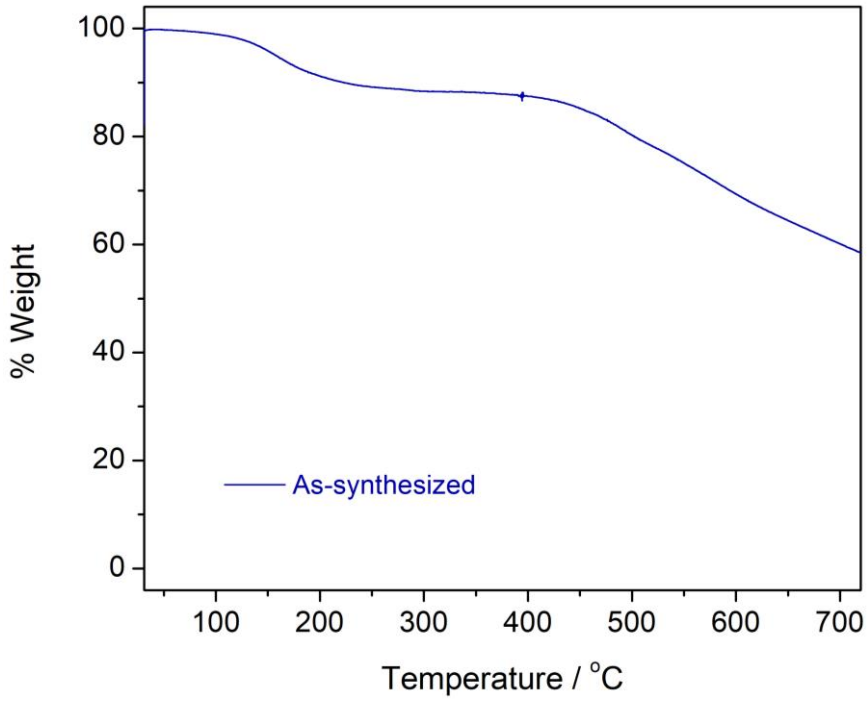

Figure S7: TGA profile for compound **IPM-303**.

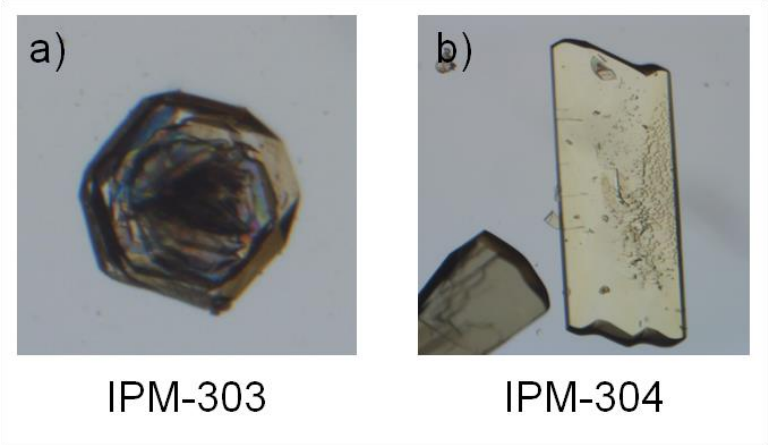

Figure S8: Photographs of crystals of a) **IPM-303** and b) **IPM-304** taken under optical microscope.

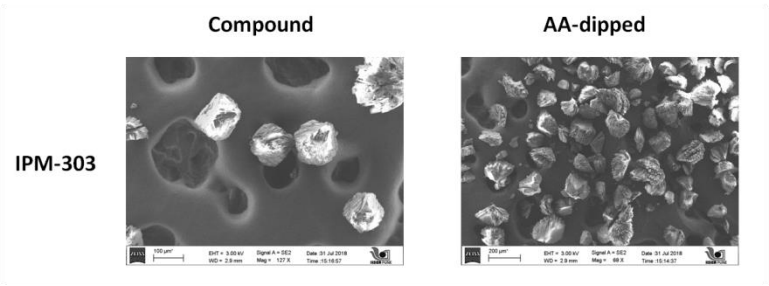

Figure S9: FESEM images for compound **IPM-303** - (left) as-synthesized phase, (right) crystals upon dipping in allyl alcohol. The images were recorded for the solid samples on carbon tape.

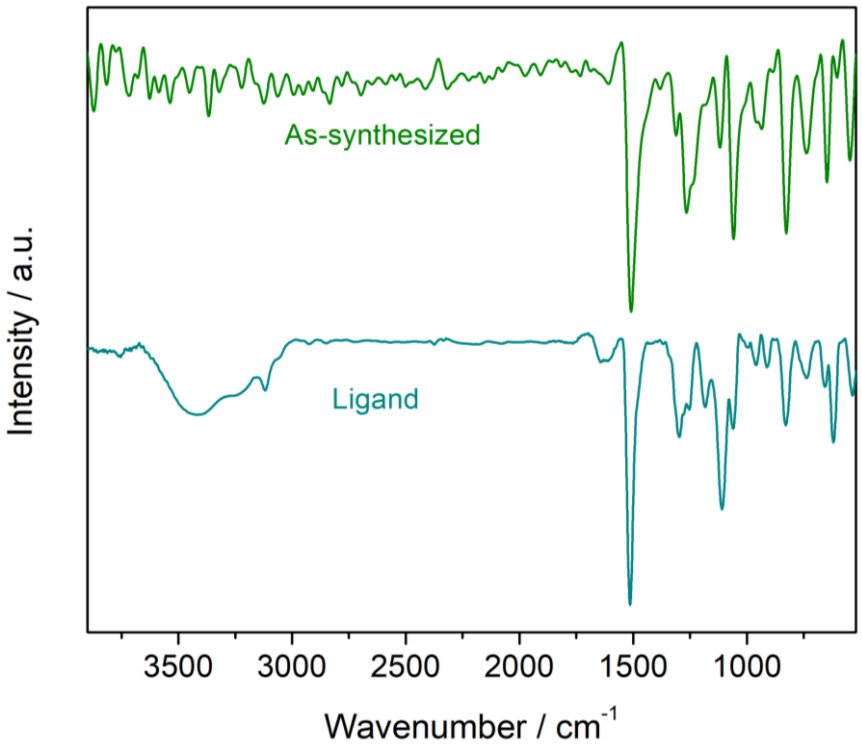

Figure S10: FT-IR spectra for the ligand and compounds **IPM-303**.

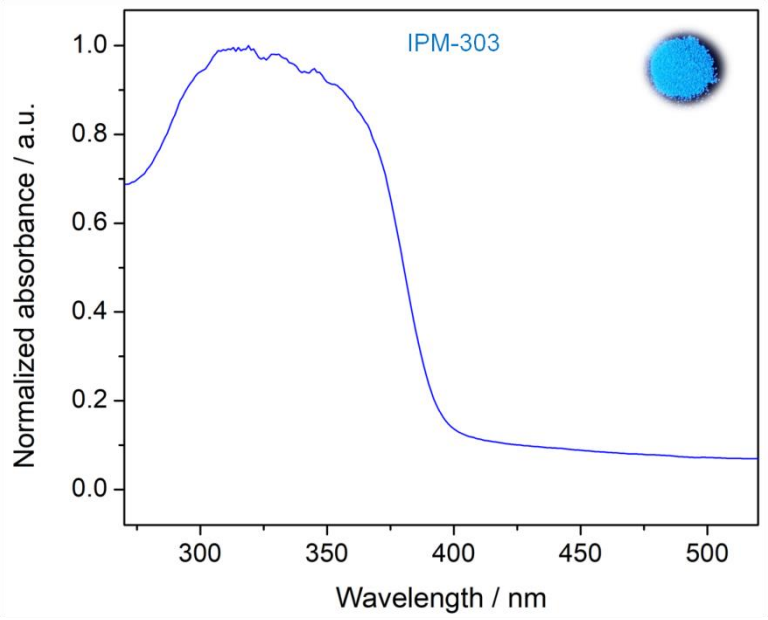

Figure S11: Solid-state UV absorbance profile for **IPM-303**. (Inset) image of illuminated MOF powder under UV lamp (365 nm).

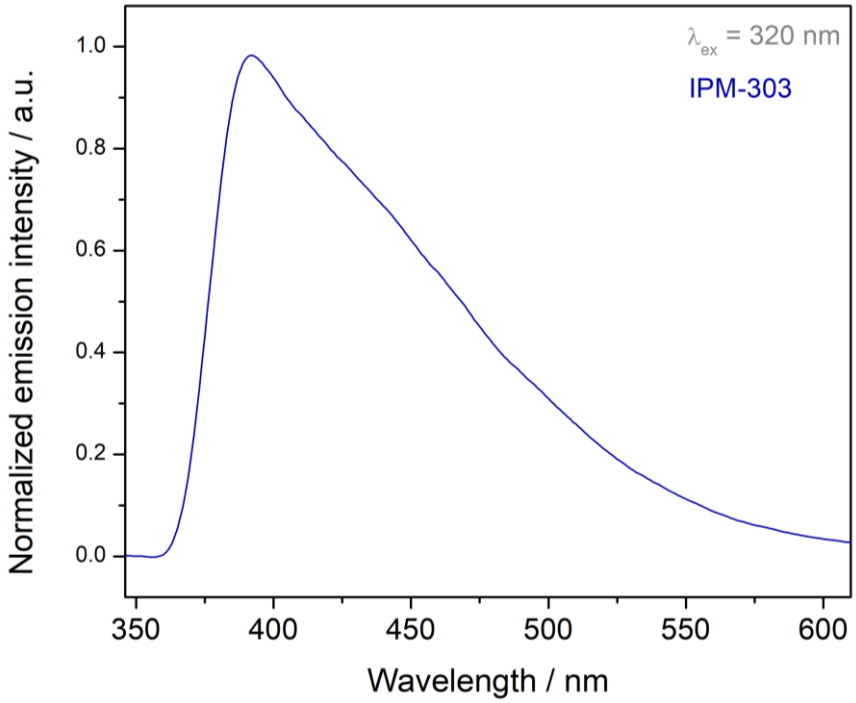

Figure S12: Fluorescence emission profile for **IPM-303** dispersed in acetonitrile (λ_{exc} = 320 nm).

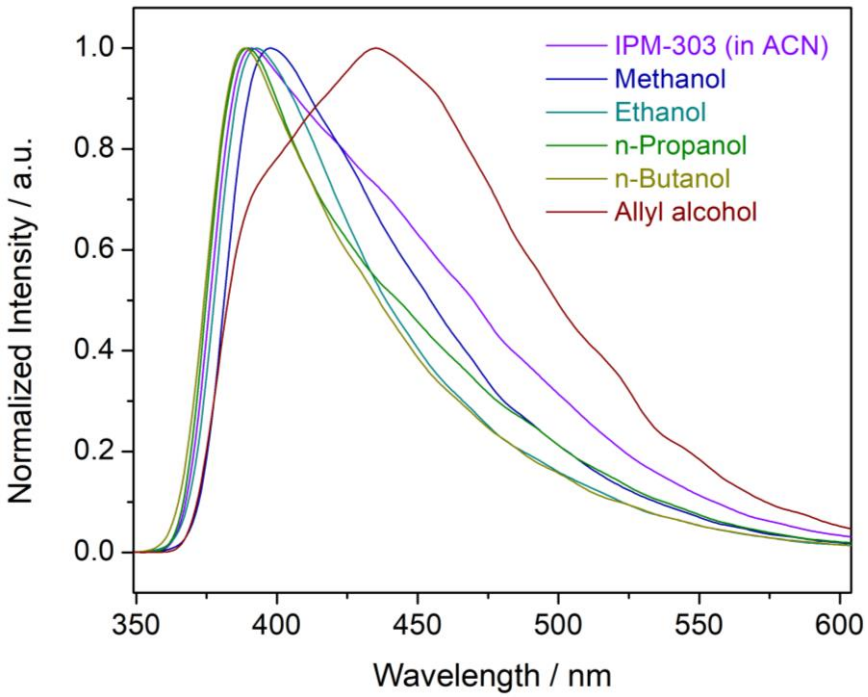

Figure S13: Normalized emission profiles for **IPM-303** when dipped in different solvents.

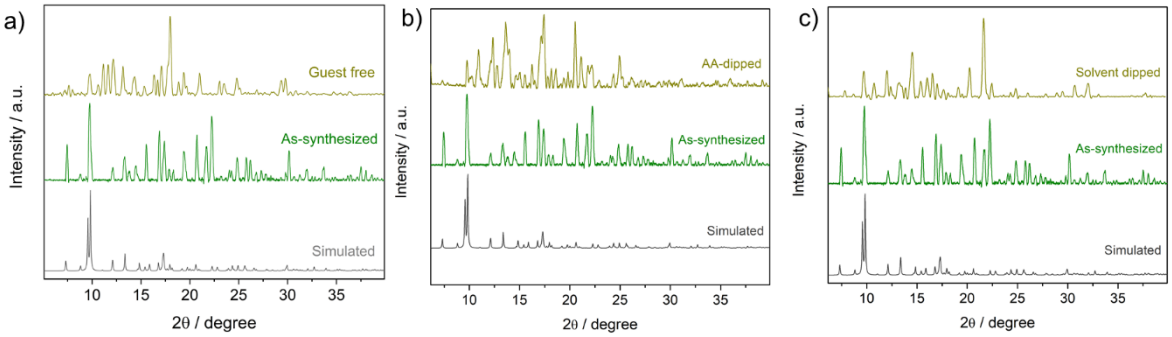

Figure S14: PXRD for **IPM-303** of a) guest free phase, b) AA-dipped phase and c) phase dipped in mixture of all other solvents used in this study.

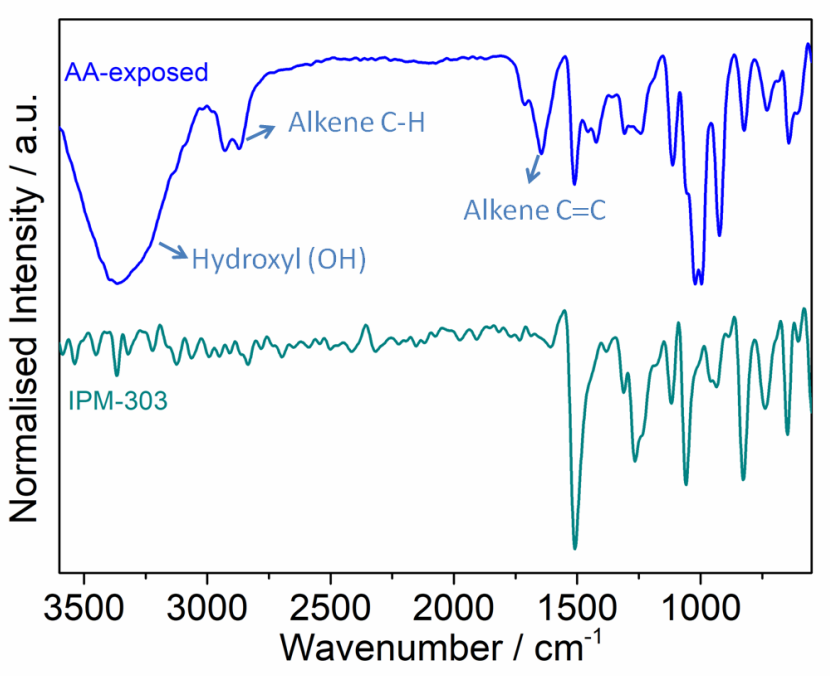

Figure S15: FTIR for the as-synthesized phase (cyan) and AA-exposed (blue).

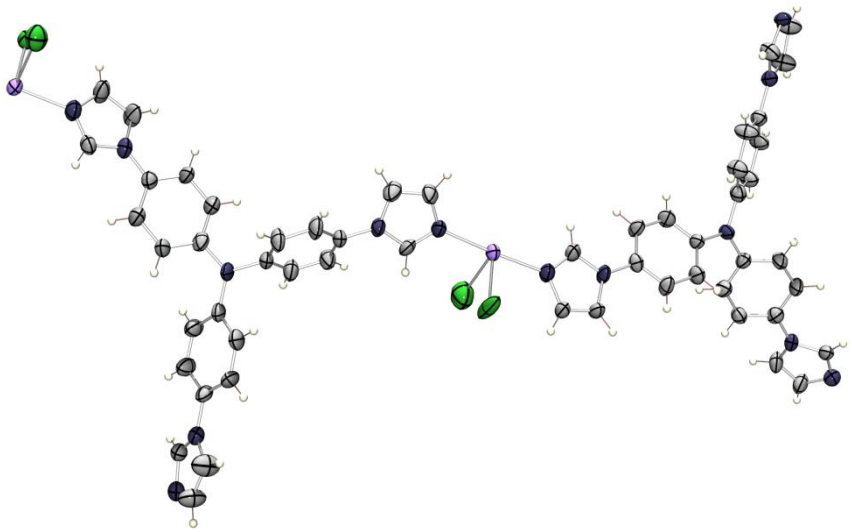

Figure S16: ORTEP diagram for **IPM-304** in thermal ellipsoids.

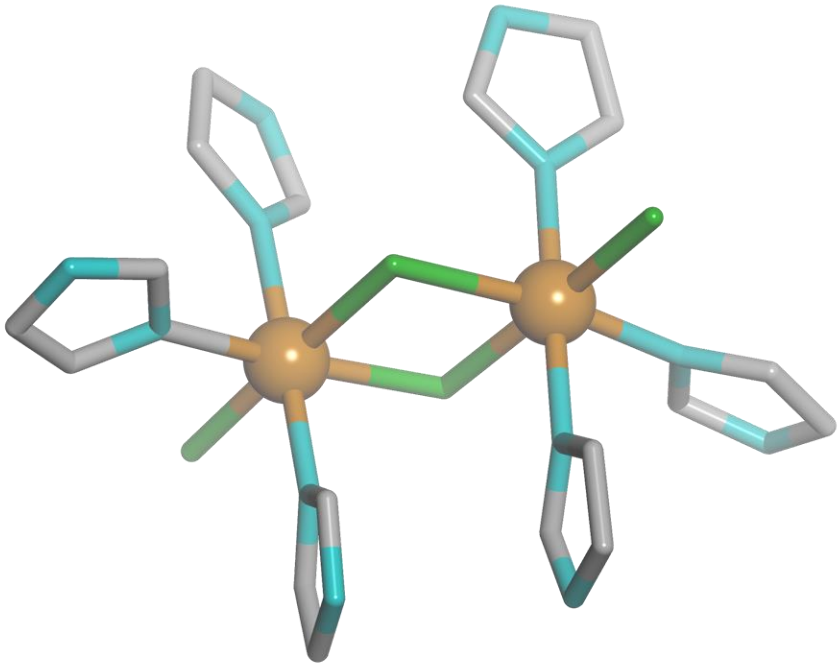

Figure S17: Coordination environment in **IPM-304** (H-atoms omitted for clarity. Colour code: C, grey; N, blue; Cl, green; Mn, orange).

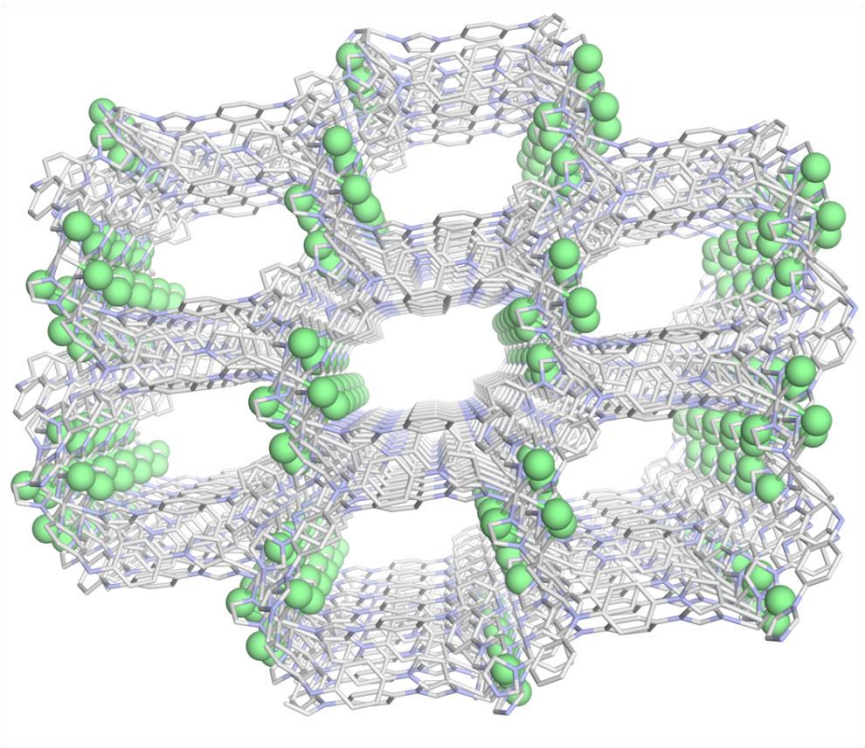

Figure S18: Packing diagram for **IPM-304** showing porous channel (H-atoms have been omitted for clarity. Colour code: C, grey; N, blue; Cl, green; Mn, light purple).

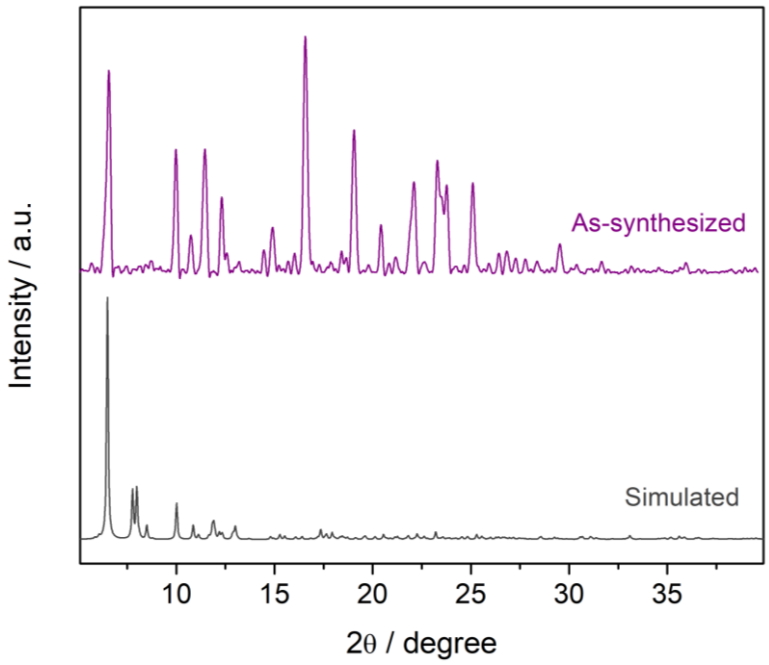

Figure S19: PXRD pattern for **IPM-304**.

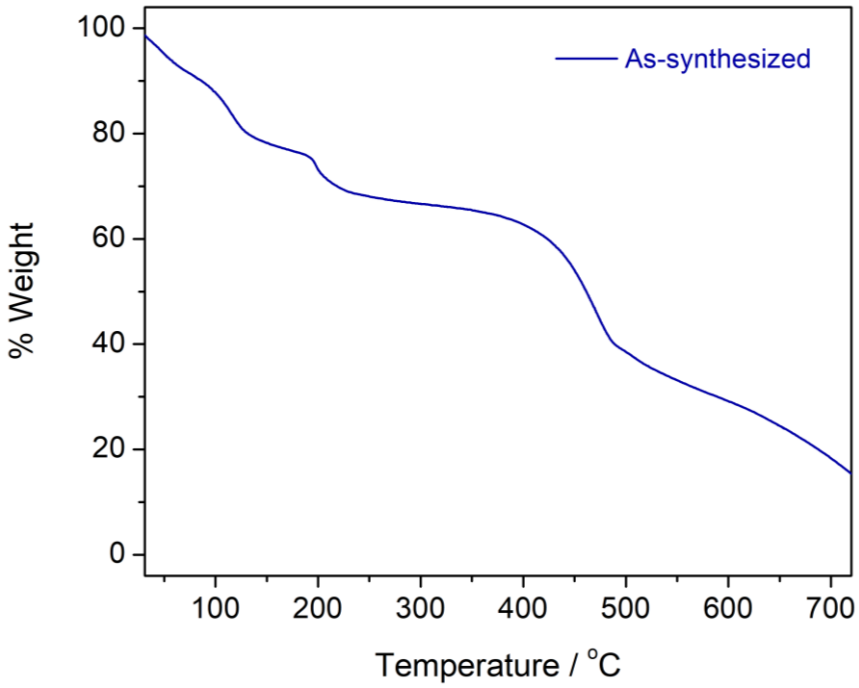

Figure S20: TGA profile for **IPM-304**.

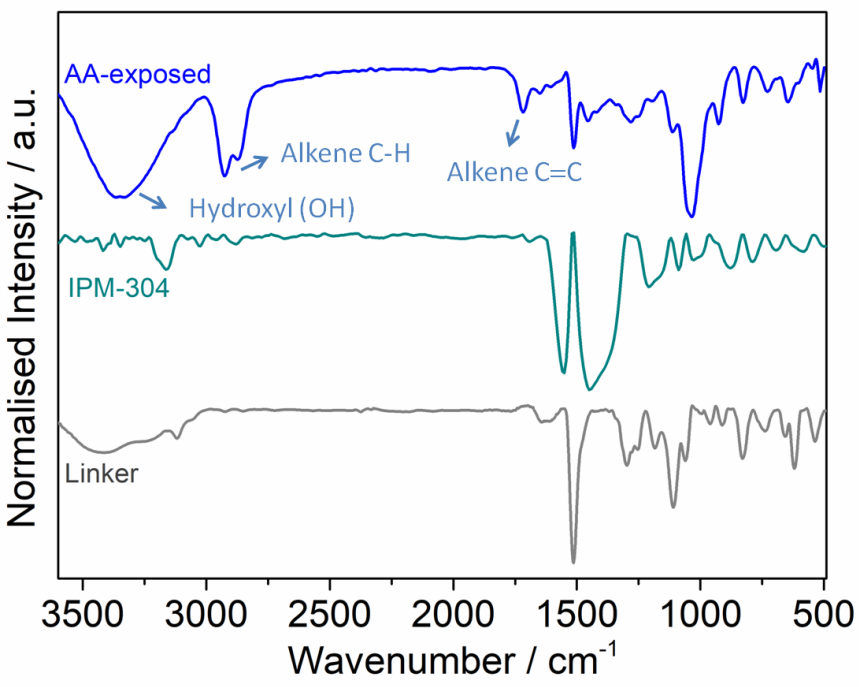

Figure S21: FTIR spectra for ligand and **IPM-304**.

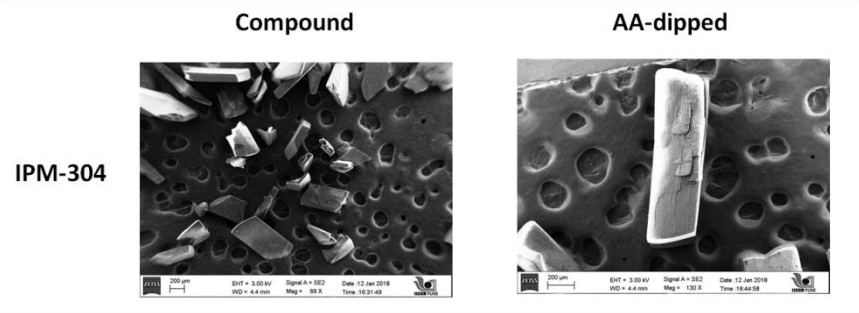

Figure S22: FESEM images **IPM-304**, (left) as-synthesized phase (right) crystals upon dipping in allyl alcohol.

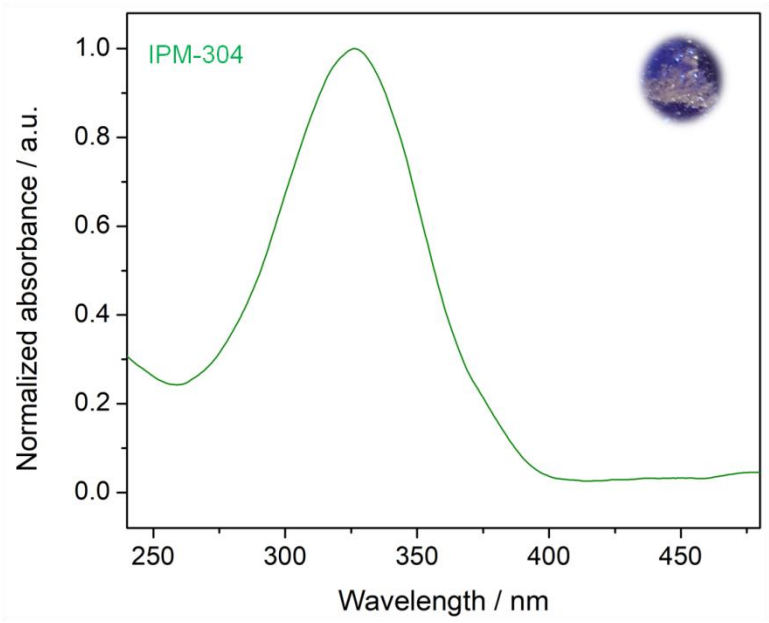

Figure S23: Solid-state UV absorbance for **IPM-304**. (Inset) Image of MOF powder illuminated under UV lamp (365 nm).

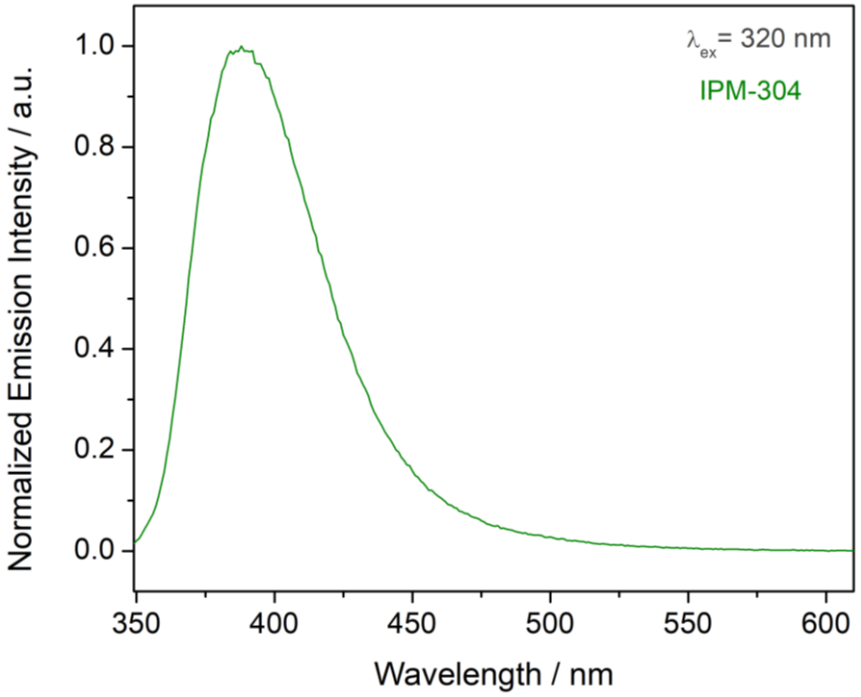

Figure S24: Fluorescence emission profile for **IPM-304** upon dispersing in acetonitrile (λ_{exc} = 320 nm).

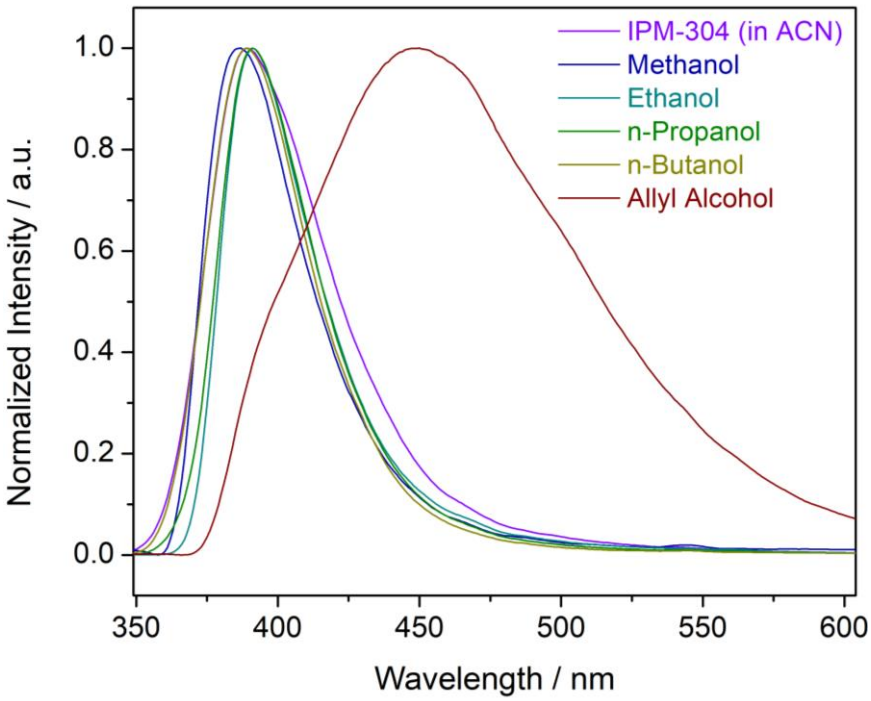

Figure S25: Normalized emission profiles for **IPM-304**, when dipped in different solvents.

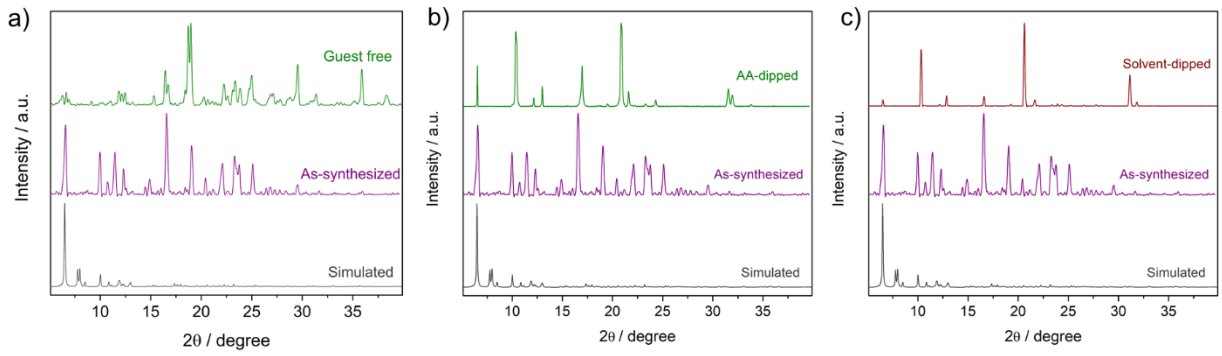

Figure S26: PXRD for **IPM-304** of a) guest-free phase, b) AA-dipped phase and c) phase dipped in mixture of all other solvents used in this study.

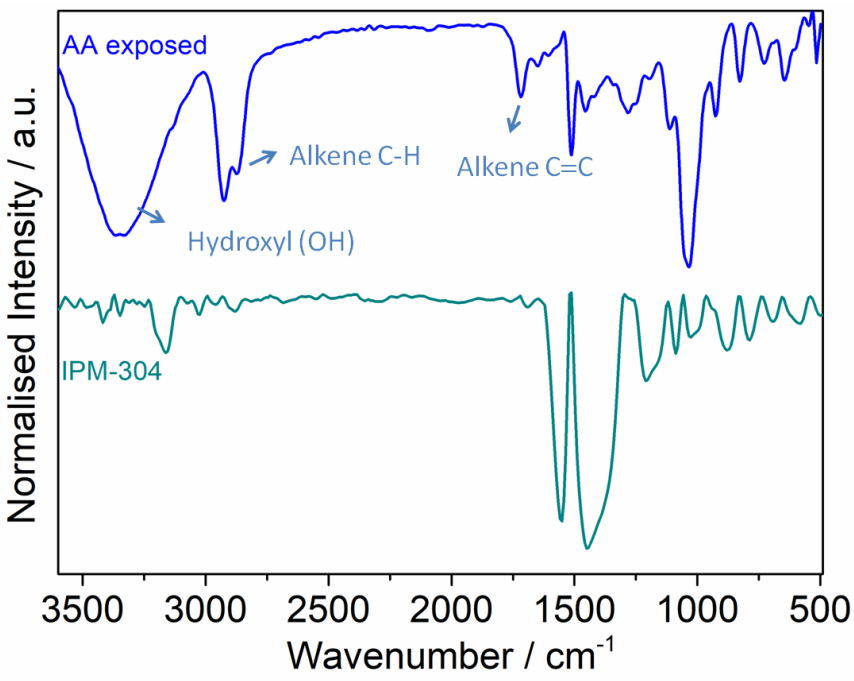

Figure S27: FTIR spectra for **IPM-304** (Cyan) and AA-exposed phase (blue).

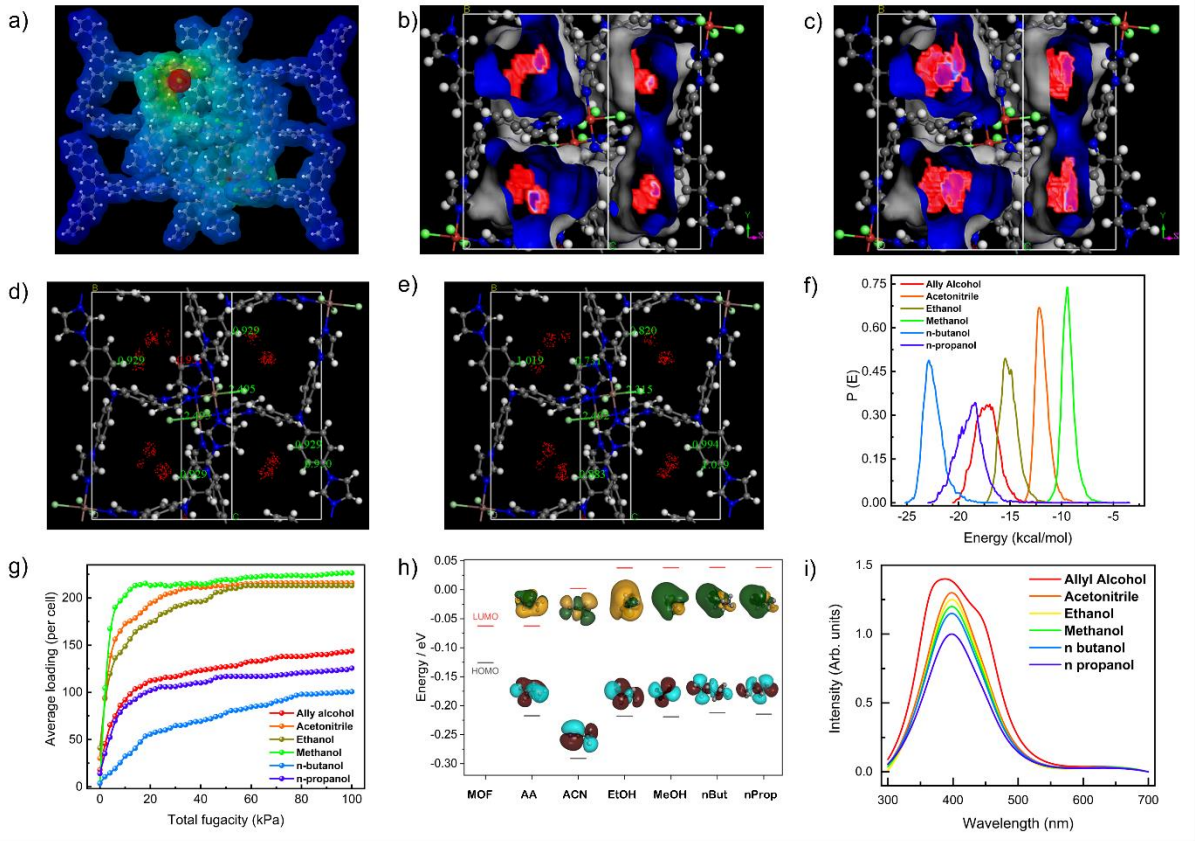

Figure S28: a) Electron density map for **IPM-303**. Figure showing Connolly surface in **IPM-303** and presence of void (represented in blue) and guest b) AA molecules (represented in red) and c) Methanol, in pore of single unit cell dimension. Change in bond distances upon interaction of AA with **IPM-303** d) before interaction and e) after interaction. f) Estimated binding energy profiles for the different molecules used in the study. g) Theoretical adsorption profile of solvents by **IPM-303** (obtained on MOF 3 x 3 x 3 supercell) in fugacity range of 0.01 kPa to 100 kPa. h) Comparative plot of HOMO-LUMO energies of MOF (single unit) and different solvents (AA – allyl alcohol, ACN – acetonitrile, EtOH – ethanol, MeOH – methanol, nBut – n-butanol, nProp – n-Propanol) . i) Theoretically predicted emission profiles for the MOF (**IPM-303**)-Guest complexes based on DFT-calculations on single unit.

Table S1. Crystal data and structure refinement for **IPM-303**.

Identification code	IPM-303	
Empirical formula	C_{27} H_{21} Cl_3 In N_7	
Formula weight	664.68	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	*P* 2_1/n	
Unit cell dimensions	a = 12.037(3) Å	α= 90°.
	b = 18.466(5) Å	β= 97.790(10)°.
	c = 16.103(4) Å	γ = 90°.
Volume	3546.1(15) $Å^3$	
Z	4	
Density (calculated)	1.245 Mg/m^3	
Absorption coefficient	0.916 mm^{-1}	
F(000)	1328	
Crystal size	0.10 x 0.08 x 0.06 mm^3	
Theta range for data collection	2.266 to 26.418°.	
Index ranges	-15<=h<=15, -23<=k<=22, -20<=l<=20	
Reflections collected	57173	
Independent reflections	7252 [R(int) = 0.1172]	
Completeness to theta = 25.242°	99.9 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7252 / 0 / 343	
Goodness-of-fit on F^2	1.261	
Final R indices [I>2sigma(I)]	R_1 = 0.1410, wR_2 = 0.2718	
R indices (all data)	R_1 = 0.1980, wR_2 = 0.3030	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.172 and -1.063 $e.Å^{-3}$	

Table S2. Crystal data and structure refinement for **IPM-304**.

Identification code	IPM-304	
Empirical formula	C_{54} H_{42} Cl_4 Mn_2 N_{14}	
Formula weight	1138.69	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	a = 15.848(9) Å	α= 86.911(17)°.
	b = 16.338(9) Å	β= 66.305(16)°.
	c = 16.560(10) Å	γ = 82.791(17)°.
Volume	3895 (4) $Å^3$	
Z	2	
Density (calculated)	0.971 Mg/m^3	
Absorption coefficient	0.497 mm^{-1}	
F(000)	1164	
Crystal size	0.16 x 0.15 x 0.14 mm^3	
Theta range for data collection	2.305 to 26.027°.	
Index ranges	-18<=h<=18, -19<=k<=19, -20<=l<=19	
Reflections collected	104477	
Independent reflections	13730 [R(int) = 0.1047]	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.0258 and 0.0106	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	13730 / 0 / 668	
Goodness-of-fit on F^2	1.143	
Final R indices [I>2sigma(I)]	R_1 = 0.1194, wR_2 = 0.3149	
R indices (all data)	R_1 = 0.1597, wR_2 = 0.3372	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.776 and -0.909 $e.Å^{-3}$	