SUPPLEMENTARY INFORMATION

Structural adaptation in a cadmium-porphyrin MOF through solvent-driven change of interpenetration

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Geometry optimization

To assess the structural effect of periodic geometry optimization, Figure S1 shows overlays of the experimentally determined structures with their fully optimized counterparts. In both UB-MOF-1 and ESRF-MOF-1, the agreement is very high, demonstrating that the optimized geometries reproduce the experimental structures very closely.

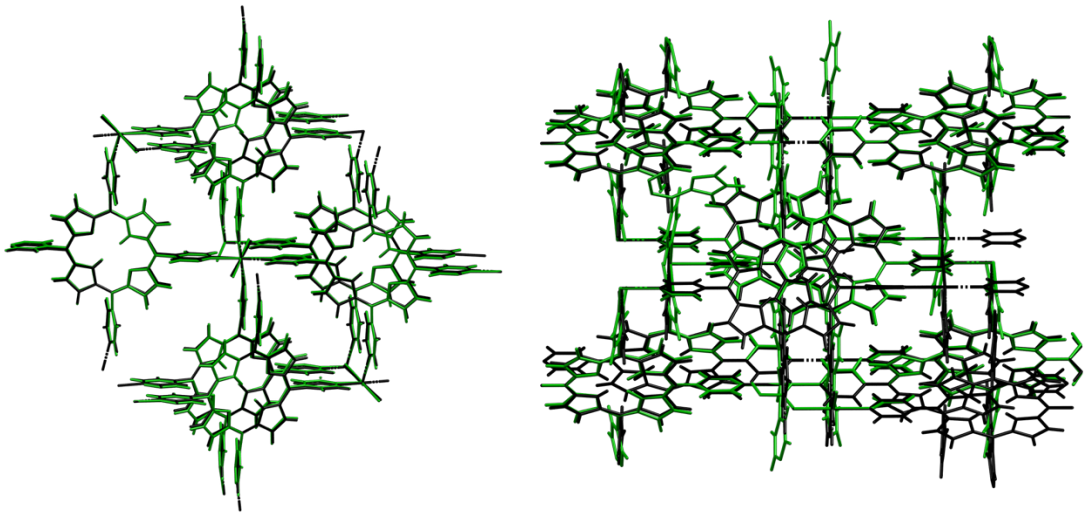

Figure S1. Overlay of experimental (black) and geometry-optimized (green) structures. Left: UB-MOF-1; right: ESRF-MOF-1.

Periodic DFT results

Table S1 lists total energies per crystallographic unit cell. ESRF-MOF-1 contains two identical interpenetrated nets and has formula unit $Z=2$. To enable a direct comparison with the stoichiometry of UB-MOF-1 (Z=1), we also report the energy of ESRF-MOF-1 divided by two. With this convention, ½ ESRF-1 is 0.043 Ha (112.8 kJ mol^{-1}) more stable than UB-MOF-1, indicating that the interpenetrated framework is thermodynamically preferred once solvent is removed.

The stabilizing interaction energy of solvated UB-MOF-1 (guest-filled) was computed as the difference between the total energy of the solvated framework and the sum of the energies of the empty UB-MOF-1 unit cell and of its isolated solvent molecules (four 3-chloroaniline (3-CA) and two 1,1,2,2-tetrachloroethane (TCE) per unit cell). With this definition, the interaction energy amounts to -0.295 Ha (-765.6 kJ mol^{-1}) per unit cell.

PLATON SQUEEZE analysis indicates 100 residual electrons per unit cell in the voids. Since there are four voids, each contains 25 electrons, which corresponds to ~0.4 3-chloroaniline molecules per void. Modelling of this residual density does not reveal any connected network that would resemble ordered 3-CA molecules. Nonetheless, we cannot exclude the possibility that the MOF is not fully desolvated, with some disordered guests remaining beyond the resolution limit. The residual density is not assigned to TCE, given its much lower evaporation point. To account for this, we also modelled the solvent interaction energy for a partially desolvated case: the total energy of UB-MOF-1 containing four 3-CA and two TCE molecules minus the energy of UB-MOF-1 still containing two of its original 3-CA molecules (≈0.4 per void) minus the energies of the two removed 3-CA and two TCE molecules. This gives an interaction energy of -458.1 kJ mol^{-1}.

Structure	**Energy per unit cell [Hartree] (kJ mol^{-1})**
UB-MOF-1 (empty)	-797.529 Ha
ESRF-MOF-1	-1595.145 Ha
1/2 ESRF-MOF-1	-797.572 Ha
Difference (½ ESRF-MOF-1 – UB-MOF-1)	-0.043 Ha (-112.8 kJ mol^{-1})
UB-MOF-1 (filled)	-1193.359 Ha
4 3-chloroaniline (3-CA)	-250.553 Ha
2 Tetrachloroethane (TCE)	-144.985 Ha
Binding energy	-0.295 Ha (-765.6 kJ mol^{-1})
UB-MOF-1 (partially-filled)*	-1067.974 Ha
2 3-chloroaniline (3-CA)	-125.285 Ha
2 Tetrachloroethane (TCE)	-144.985 Ha
Binding energy	-0.174 Ha (-458.11 kJ mol^{-1})

* Partial case considers residual ~0.4 3-CA molecules per void (modelled as two per unit cell) remaining after desolvation.

Table S1. Top: Periodic DFT energies of UB-MOF-1, ESRF-MOF-1, and their difference. Middle: DFT energies of solvated UB-MOF-1 and isolated solvent molecules (four 3-CA and two TCE per unit cell), with the corresponding host-guest interaction. Bottom: Analogous solvation energy for partially-filled UB-MOF-1.

Solvent desorption and crystal appearance

Solvent desorption was performed in a Memmert UM100 Laboratory oven with the vent fully opened. The top of the goniometer head was found to become in thermal equilibrium with the oven within 5 minutes, with an average heating rate of 25 °C/min. The crystal appearance remained the same before and after the heating.

Figure S2. Microphotographs of UB-MOF-1 (left) before solvent desorption, and the desolvated ESRF-MOF-1 (right) after the solvent removal.

Solvent reabsorption experiments

A single-crystal of ESRF-MOF-1 was soaked in H_2O, ethanol, methanol and 1% w/w 3-chloroaniline solution in MeOH, respectively, for 3 hours at room temperature. After each soaking process, the unit cell parameters of the crystal have been measured using short XRD measurement (circa 50 reflections per dataset):

	MeOH	**EtOH**	**H_2O**	**1% 3-CA in MeOH**
a [Å]	12.813(1)	12.810(1)	12.818(1)	12.815(1)
b [Å]	15.673(2)	15.677(2)	15.669(2)	15.677(3)
c [Å]	20.311(4)	20.313(4)	20.310(4)	20.311(4)
V [Å^3]	4079(1)	4079(1)	4079(1)	4080(1)
number of reflections	51	49	49	48

Table S2. Lattice parameters of ESRF-MOF-1 measured after soaking procedure in various solvents

Additionally, we performed an experiment in which we soaked the crystal (2.8 mg) in 2.15 mmol/L 3-chloroaniline in MeOH solution at 50 °C for 22 hours. We collected the UV-vis spectra of the solution before and after the soaking (Figure S2). The absorbance change at the maximum of absorption of 3-chloroaniline at 293 nm was -0.8 %. Therefore, the interaction between MOF and solute is not significant, if there is any interaction (absorption) at all.

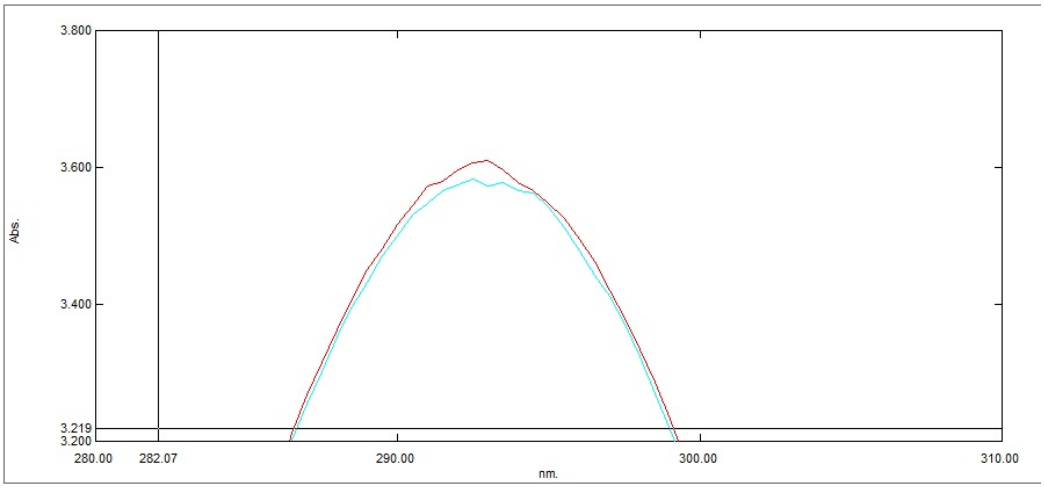

Figure S3. Changes in 3-TCE absorbance before (red) and after (light blue) soaking a crystal of ESRF-MOF-1

Visualization of structural voids

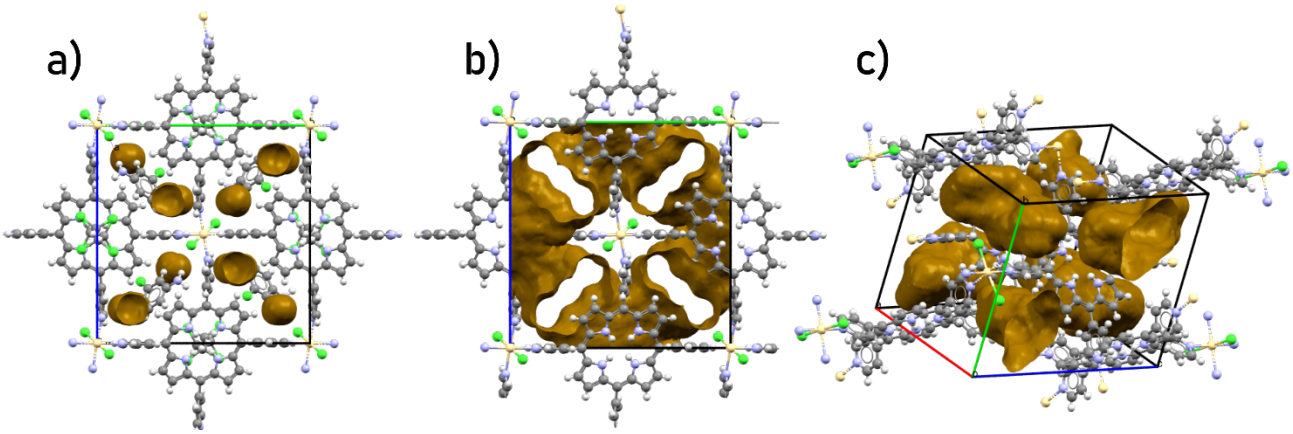

Figure S4. Structural voids visualized in a) UB-MOF-1, b) UB-MOF-1 with manually removed solvent, c) ESRF-MOF-1. The orange void contact surfaces were plotted at 1.2 Å probe radius with a grid spacing of 0.2 Å in Mercury.