Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supplementary Information

Rational Design of Carborane-Based Cu_2-paddle wheel Coordination Polymers for Increased Hydrolytic Stability

Zhen Li,[a] Duane Choquesillo-Lazarte,[b] Julio Fraile,[a] Clara Viñas,[a] Francesc Teixidor,[a] José G. Planas*[a]

[a] Institut de Ciència de Materials de Barcelona (ICMAB-CSIC) Bellaterra, Spain.

E-mail: jginerplanas@icmab.es

[b] Laboratorio de Estudios Cristalográficos, IACT, CSIC-Universidad de Granada, Avda. de las Palmeras 4, 18100 – Armilla, Granada, Spain

Figure S1. Comparison of IR spectra for **H_2L2** (red) and **2** (black).

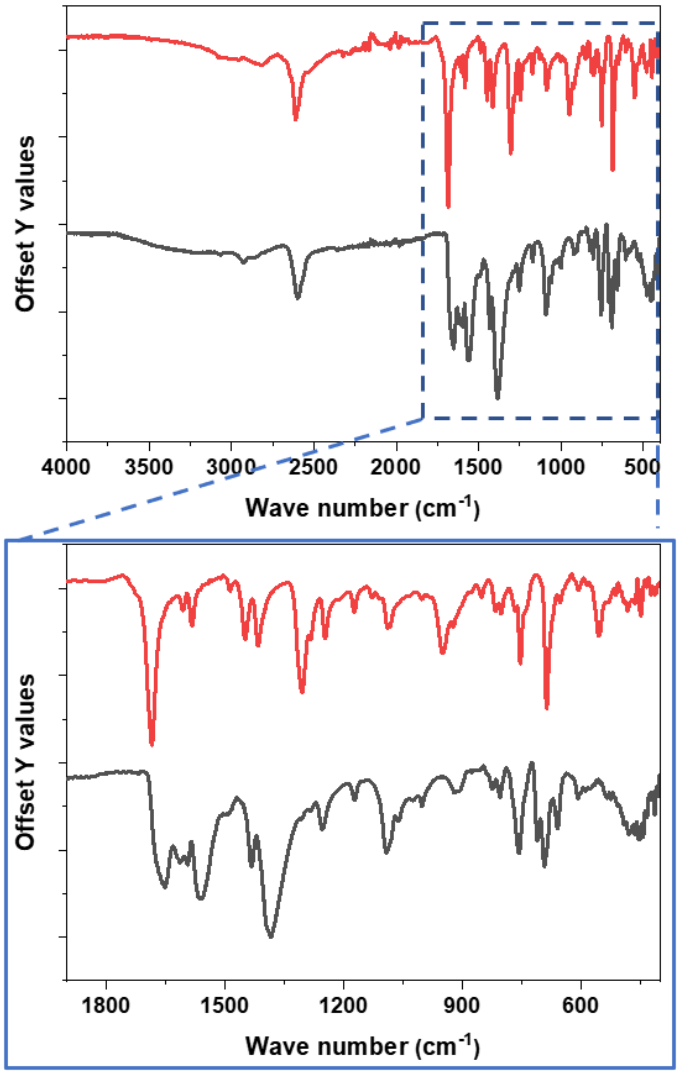

Table S1. Crystallography.

Table S1. Crystal and Structure Refinement data for **2**	
Empirical formula[a]	C37 H50 B20 Cu2 N O11
Formula weight	1028.06
Crystal system	Monoclinic
Space group	*P2/c*
Wavelength (Å)	1.54178 Å
Temperature	298(2) K
a (Å)	a = 26.912(4)
b (Å)	b = 7.1244(9)
c (Å)	c = 28.323(4)
β (deg)	109.957(5)
V ($Å^3$)	5104.4(12)
Z	4
$\rho_{(calc)}$ (g/cm^3)	1.338
F (000)	2100
θ range (deg)	6.212-66.423
Absorp.coeff. (mm^{-1})	1.461
Ind refln (R_{int})	8905 0.1742
Goodness-of-fit on F^2	0.950
R_1[b] (I > 2σ(I)) R_1 (all data) wR_2[c] (I > 2σ(I)) wR_2 (all data)	0.0694 0.1436 0.1695 0.2078

[a] Based on the formula without uncoordinated solvent molecules.

[b] $R_1 = \Sigma(||F_0|-|F_C||)/\Sigma|F_0|$.

[c] $wR_2 = [\Sigma w(|F_0|^2-|F_C|^2)^2/\Sigma w(F_0^2)]^{1/2}$.

Table S2. Selected distances (Å) for **1** and **2**			
Crystals	**Cu-Cu**	**Cu-O_2C**	**Cu-Osolv.**
1	2.607(2) 2.641(2)	1.941(4) 1.948(4) 1.959(5) 1.966(4) 1.972(4) 1.974(4) 1.981(5) 1.991(4)	2.111(5) 2.138(4)
2	2.621(1)	1.952(5) 1.954(4) 1.962(5) 1.967(4) 1.972(5) 1.979(4) 1.982(4) 1.984(5)	2.154(5) 2.158(5)

Figure S2. Comparison of calculated (black) and experimental (red) PXRD of **2**.

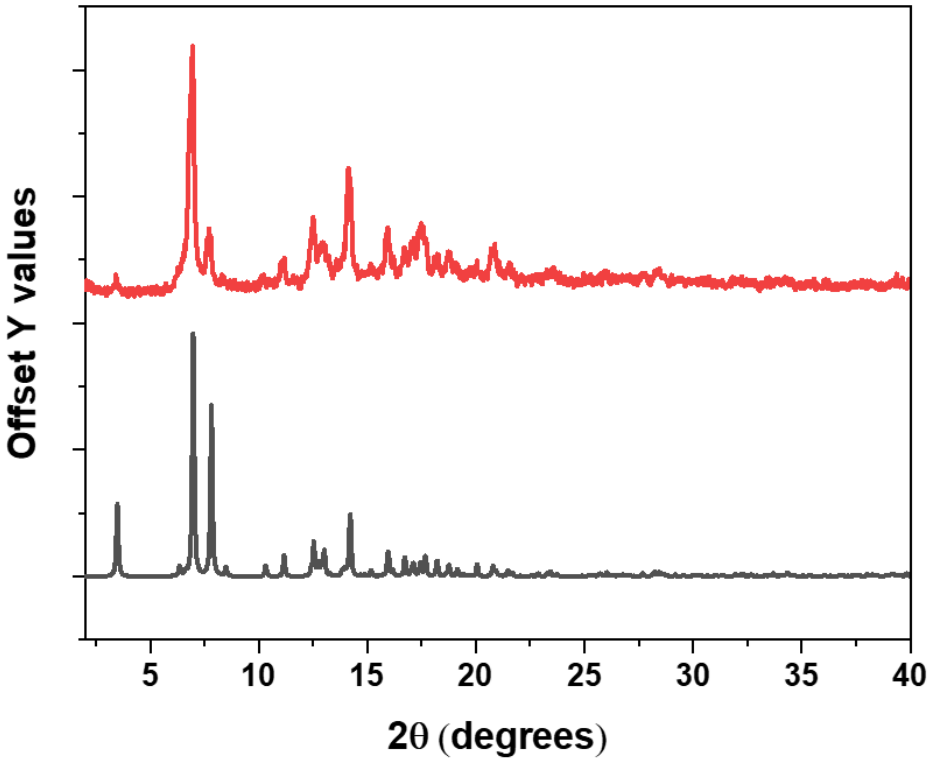

Figure S3. DTA curves for compound **2**.

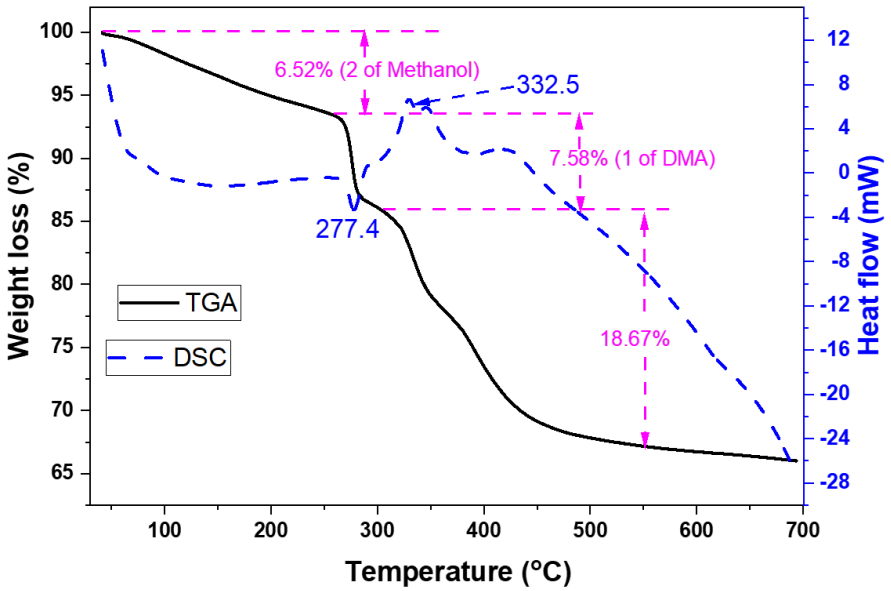

Figure S4. N_2 sorption at 77 K (A) and CO_2 sorption isotherms at 273K (B) for activated **2**.

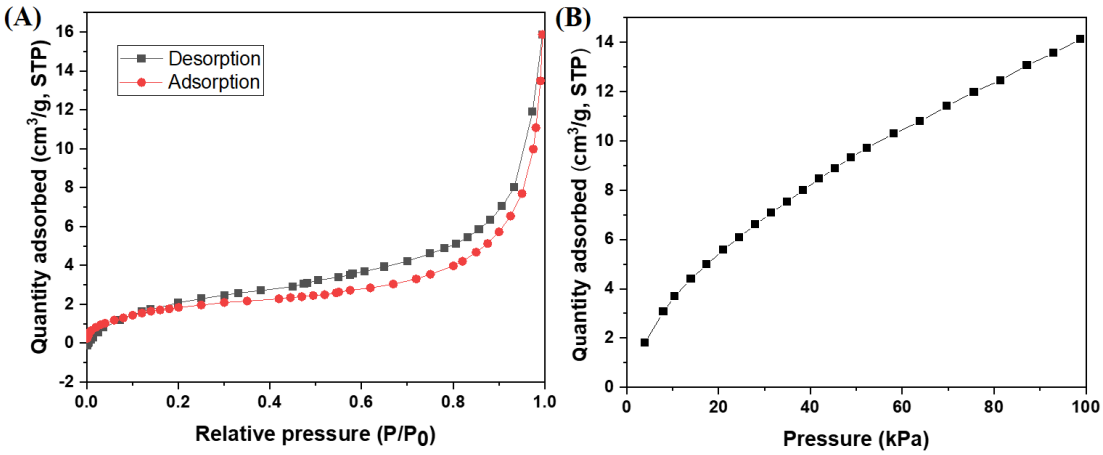

Figure S5. A view of the X-ray structure of **2** showing the two observed different ligand conformations.

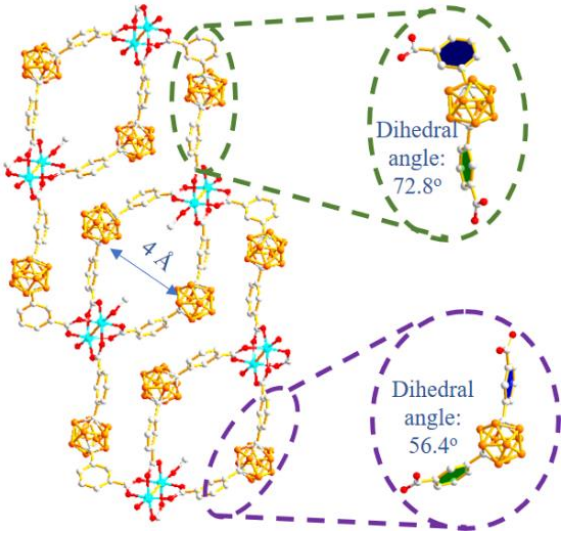

Figure S6. Topology of **2**.

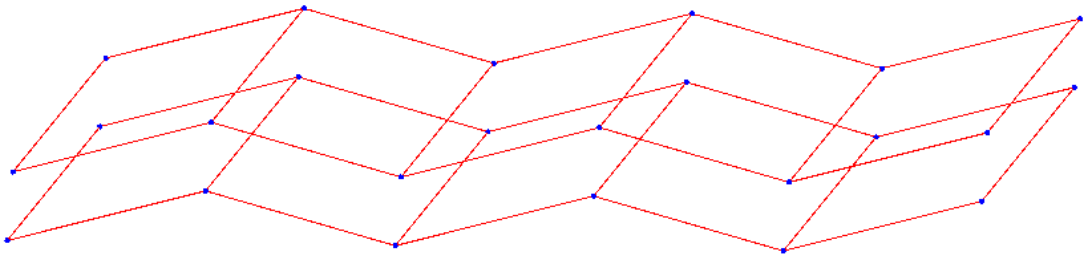

Figure S7. Two perpendicular views of the stacked 1D chains to provide the 3D structure of **2**. 1D chains are colored red or blue for clarity.

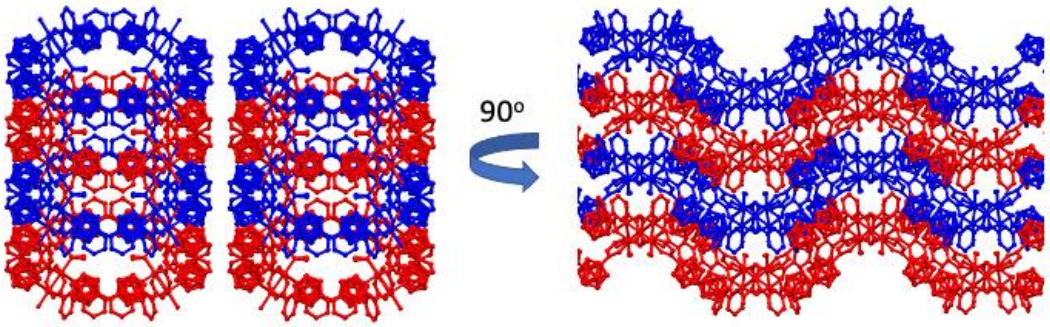

Figure S8. A comparative view of the crystal structures of **1** (left) and **2** (right). (A) different configurations of carborane ligands. (B) View of the Cu_2-paddlewheel units with carborane ligand coordination. (C) Perpendicular views of the extended structures showing the 2D networks and 1D belt topology, respectively; (D) Views along a-axial direction illustrating the corrugated configuration of Cu-MOFs. (E) View of the packing structures for the Cu-MOFs showing the staking of layer/belt structures in which the contiguous layers/belts were identified by various colors. Coordinated solvent molecules and H atoms are omitted for clarity. Color code: B brown; C grey; O red; N blue; Cu cyan.

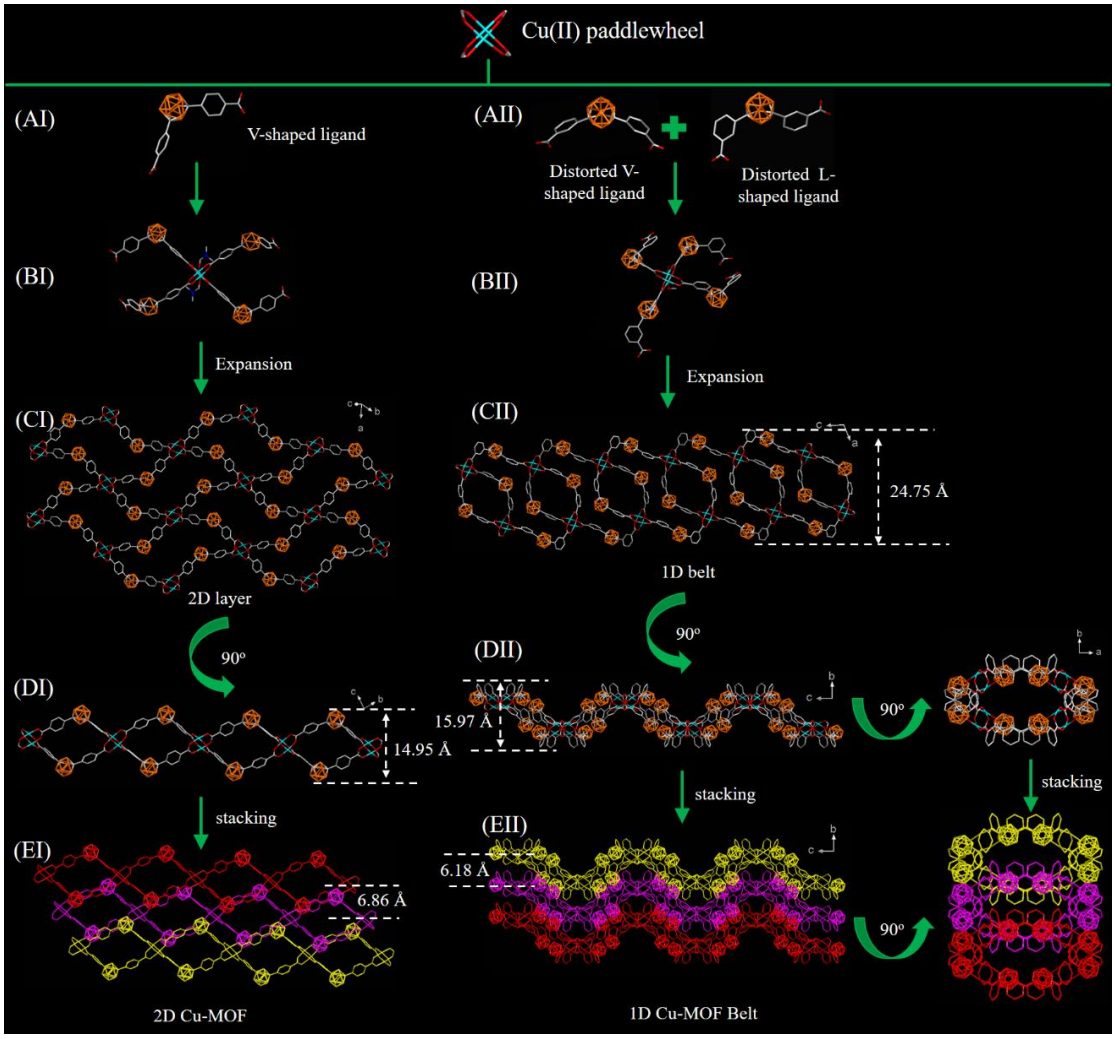

Figure S9. Photographs of water suspensions of crystals of **1** (A) or **2** (B) after being immersed in water for 7 days and 14 days.

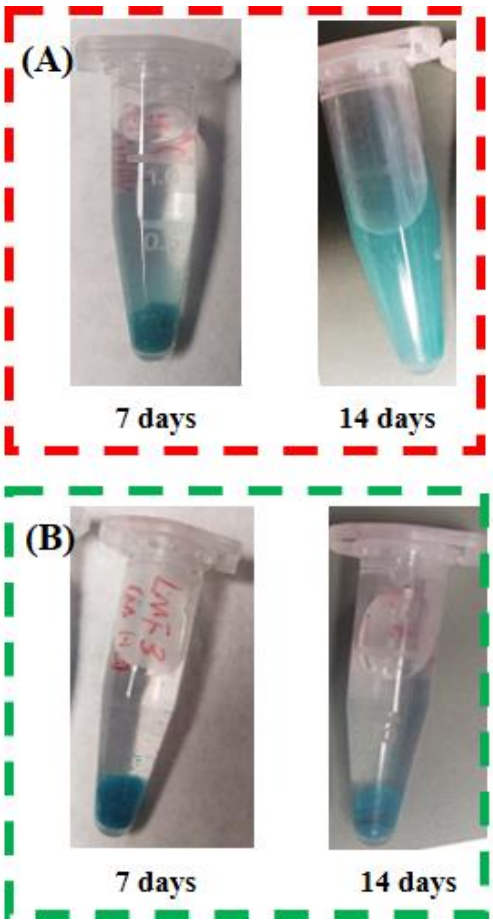

Figure S10. PXRD of **2** after being immersed in various solvents for 24h.

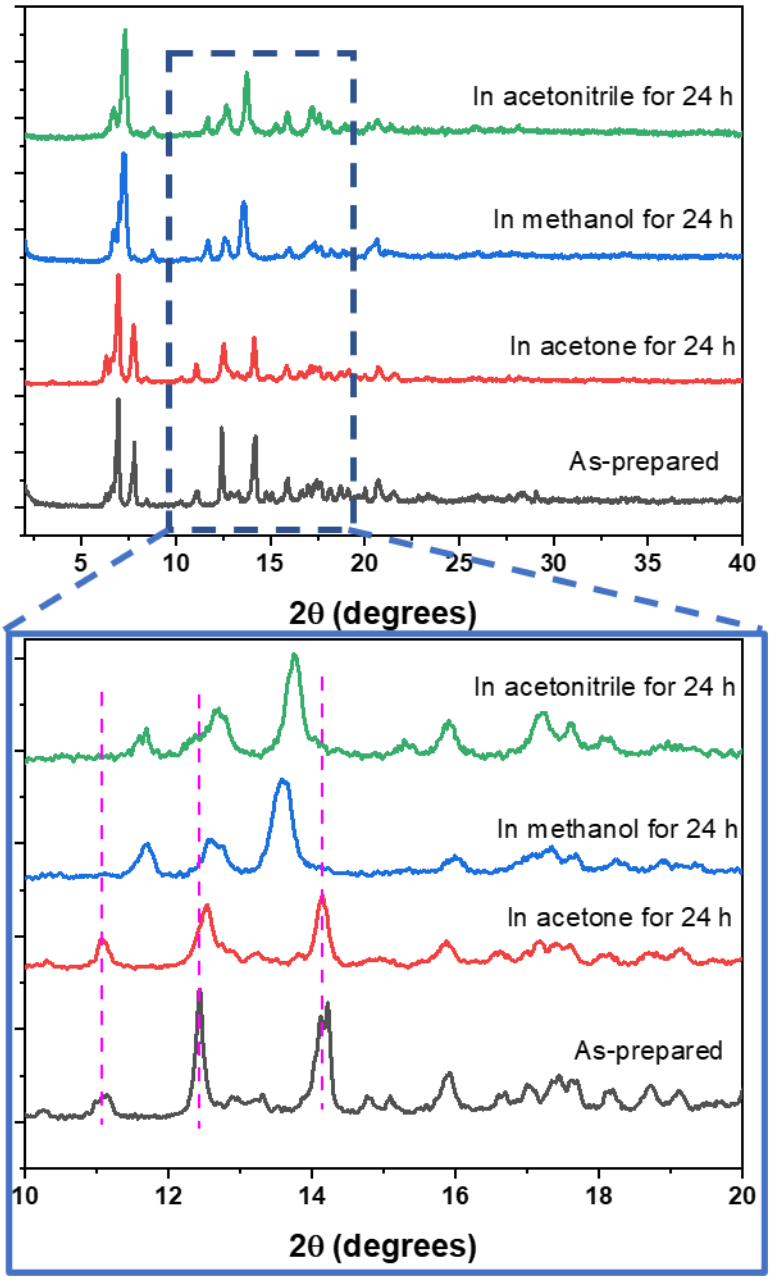

Figure S11. PXRD of **2** after being immersed in water for various times and the corresponding optical images of selected crystals.

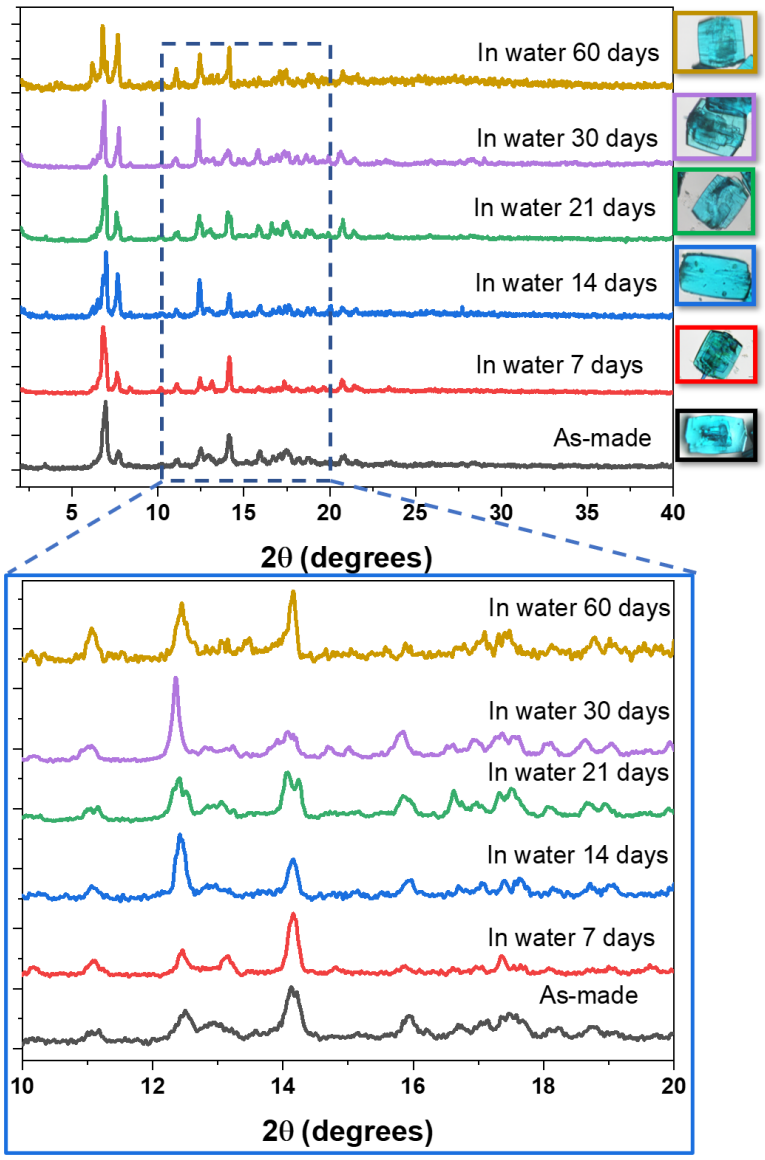

Figure S12. Optical images of crystals of **2** after being immersed in water for 30 (A) and 60 (B) days.

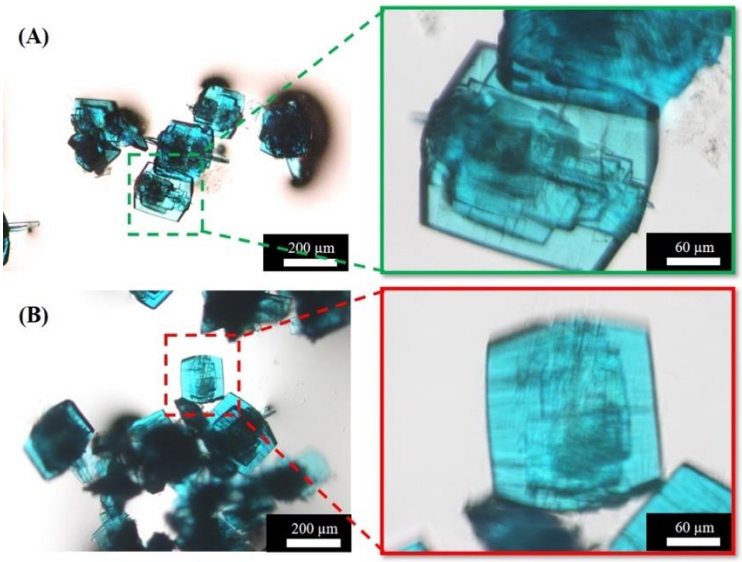

Figure S13. PXRD patterns of crystals of **2** after being immersed in aqueous KOH or HCl solutions for 24 h.

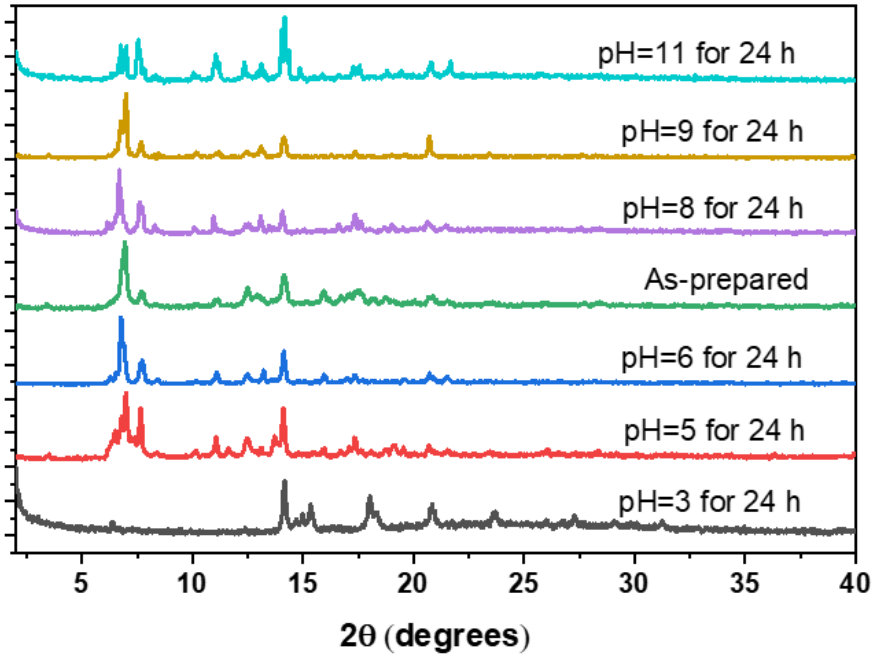

Figure S14. Optical images of crystals of **2** after being immersed in aqueous KOH or HCl solutions for 24 h.

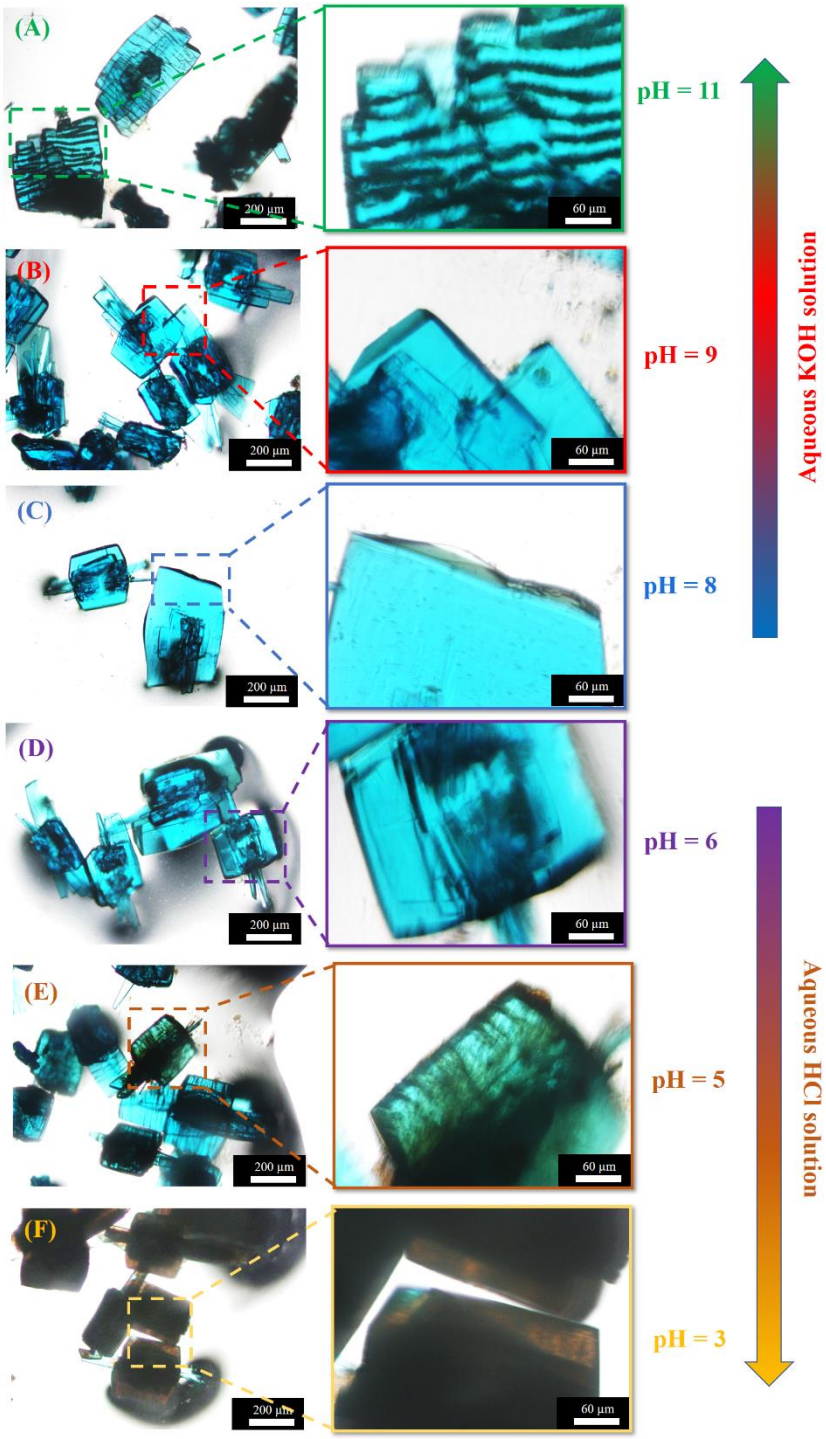

Table S3. Comparison of catalytic results of Cu-MOFs at different time intervals

Entry	Catalyst[a]	Time (min)	Conversion[b]
1	**1**	30	80
2		60	100
3	**2**	30	70
4		60	100
6	none	60	6

[a] Reaction conditions: hexylamine (2.0 mmol); acrylonitrile (2.2 mmol); catalysts (1%); methanol (4 mL); room temperature. [b] Estimated by NMR.

References

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