Supporting Information

Stepwise single-crystal-to-single-crystal phase transition in copper-based coordination polymers triggered by solvent release

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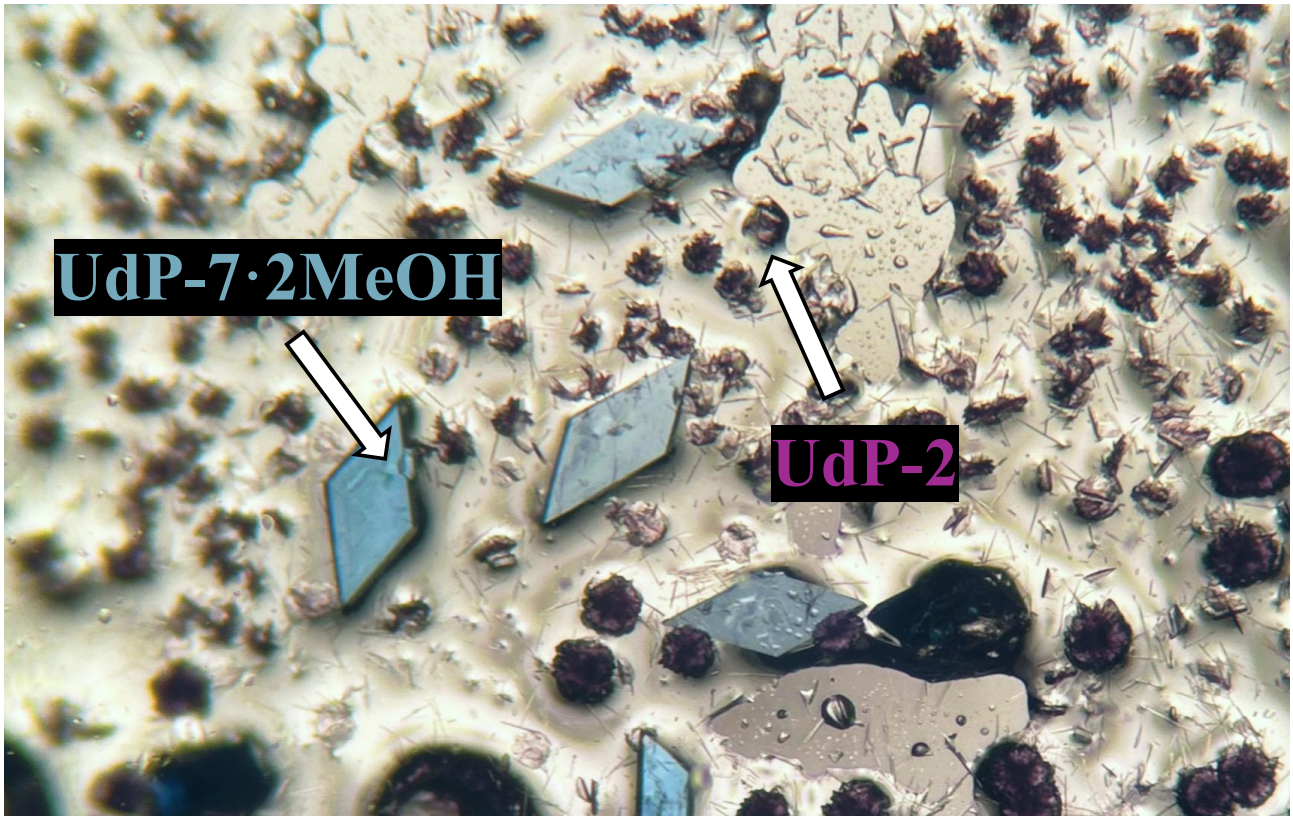


Figure S1. Image of crystals of **UdP-2** and **UdP-7·2MeOH**

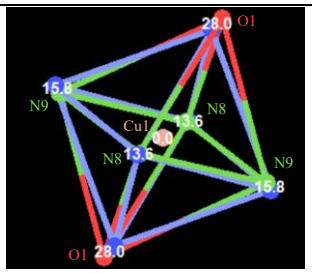
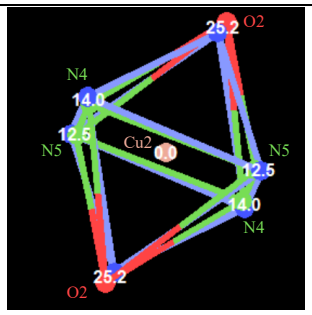
In all the structures presented, the metal centers adopt distorted octahedral geometries, more accurately described as bipyramidal parallelograms, as indicated by the δ parameter calculated using the *Polynator* software.[1]

The δ parameter is defined as:

$$\delta = \left(\frac{\sum_i |a_i - v_i|^2}{\sum_i |a_i - c|^2} \right)^{1/2}$$

where a_i corresponds to the position vector of atoms in the experimental structure (nitrogen or/and oxygen atoms), v_i refers to the vectors of the idealized reference polyhedron (i.e., regular octahedron as shown), and c is the centroid of the coordinating atoms around the copper center (Cu1 or/and Cu2). All δ values for both the octahedral and bipyramidal parallelogram geometries are reported in Table S1. Atom numbering is consistent with that in the corresponding .CIF files, and values in white indicate the deviations (in pm) from the corresponding ideal polyhedron.

Table S1. Distortion parameters for the coordination polyhedra of the Cu(II) centers in the different UdP-7 phases. δ_{oh} and δ_{bp} (where *oh* = octahedron and *bp* = bipyramidal parallelogram) were calculated from single-crystal X-ray diffraction data. In the figures, Cu atoms are shown in ochre, O atoms in red, N atoms in green, and the idealized octahedral positions in blue. Atom numbering is consistent with that reported in the corresponding CIF files. White values indicate the deviations (in pm) from the ideal polyhedron.

Structures	Central atom	δ_{oh}	δ_{bp}	Coordination polyhedron
UdP-7·2MeOHα	Cu1	9.331	0.091	
	Cu2	8.435	0.429	

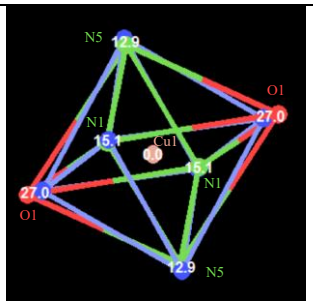
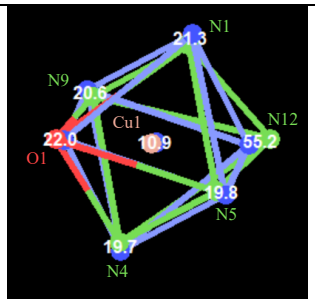
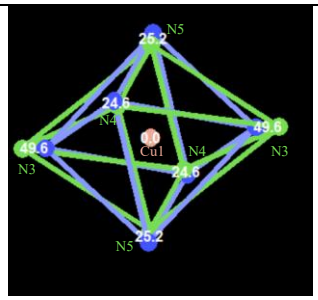
UdP-7·2MeOHβ	Cu1	8.955	0.074	
UdP-7·MeOH	Cu1	13.350	5.541	
UdP-7	Cu1	15.336	0.689	

Table S2. Views of the unit cell of the all four phases along the crystallographic axes *a*, *b*, and *c*, as obtained from single-crystal X-ray diffraction data. Hydrogen atoms have been omitted for clarity.

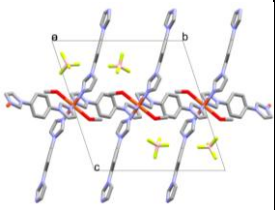
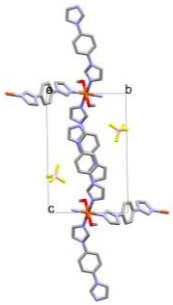
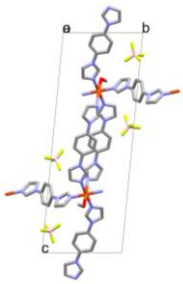
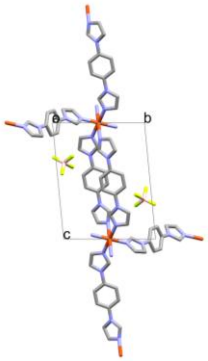
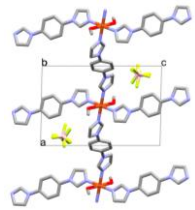
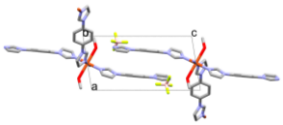
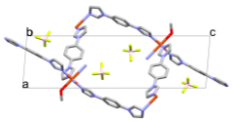
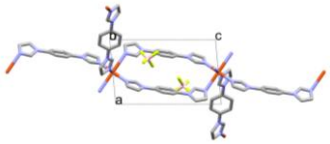
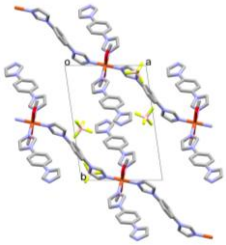
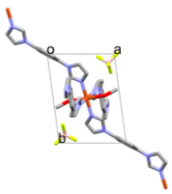
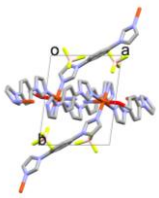
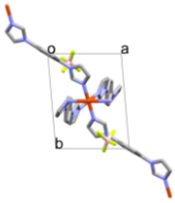
axis	**UdP-7·2MeOHα**	**UdP-7·2MeOHβ**	**UdP-7·MeOH**	**UdP-7**
a				
b				
c				

Table S3. Selected bond lengths (Å) and bond angles (°) involving the copper(II) center in the **UdP-7·2MeOHα** and **UdP-7·2MeOHβ** phases.

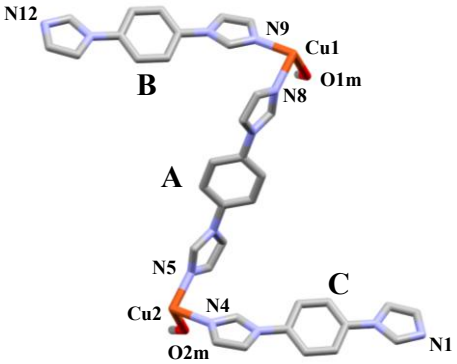
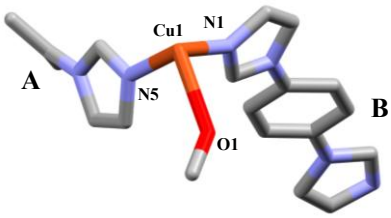
Sample	***Structure***	***Selected Cu–Ligand Distances and Angles***	***Values***
UdP-7·2MeOHα		Cu1-N8 (bib-A) (Å)	2.015(1)
		Cu1-N9 (bib-B) (Å)	2.023(2)
		Cu1-O1m (Å)	2.419(2)
		Cu2-N4 (bib-C) (Å)	2.029(2)
		Cu2-N5 (bib-A) (Å)	2.017(2)
		Cu2-O2m (Å)	2.382(2)
		N9-Cu1-N8 (°)	90.07(6)
		N9-Cu1-O1m (°)	85.39(5)
		N8-Cu1-O1m (°)	90.11(5)
		N5-Cu2-N4 (°)	89.96(6)
		N5-Cu2-O2m (°)	89.40(5)
		N4-Cu2-O2m (°)	94.17(5)
UdP-7·2MeOHβ		Cu1-N1(bib-B) (Å)	2.022(2)
		Cu1-N5(bib-A) (Å)	2.022(2)
		Cu1-O1 (Å)	2.409(2)
		N1-Cu1-N5 (°)	90.03(9)
		N1-Cu1-O1 (°)	85.88(8)
		N5-Cu1-O1 (°)	89.90(8)

Table S4. Selected bond lengths (Å) and bond angles (°) involving the copper(II) center in the **UdP-7·MeOH** and **UdP-7** phases.

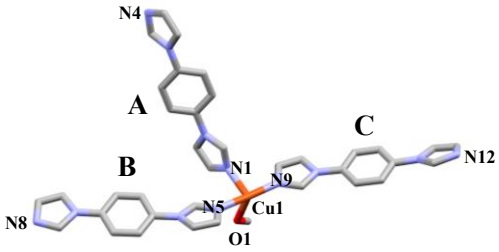
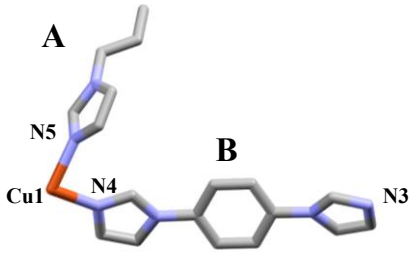
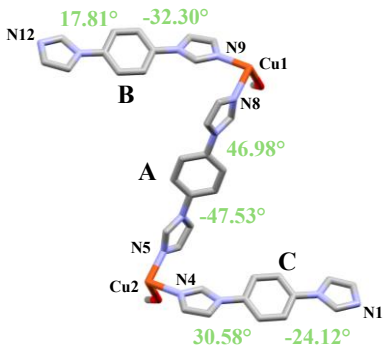
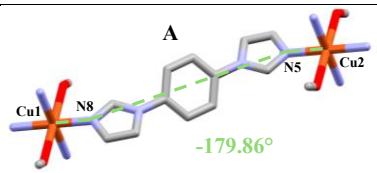
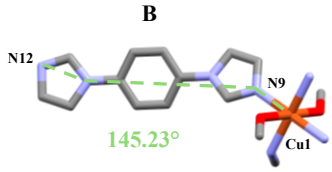
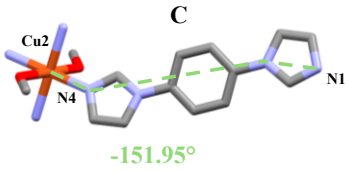
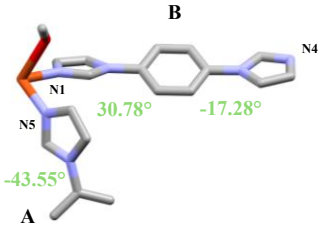
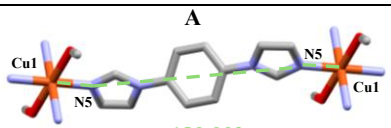
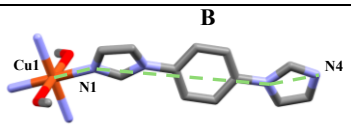
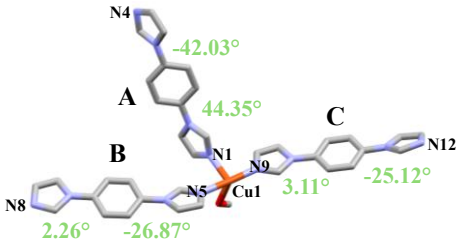
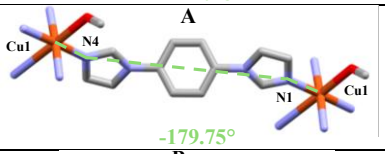
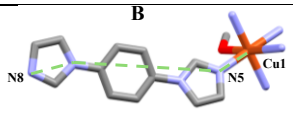
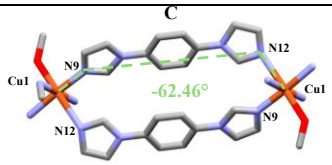
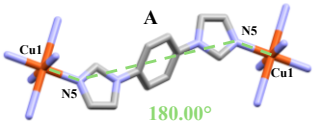
Sample	*Structure*	*Selected Cu–Ligand Distances and Angles*	*Values*
UdP-7·MeOH		Cu1-N1 (bib-A) (Å)	2.026(5)
		Cu1-N4 (bib-A) (Å)	2.012(5)
		Cu1-N5 (bib-B) (Å)	2.022(5)
		Cu1-N9 (bib-C) (Å)	2.016(6)
		Cu1-N12 (bib-C) (Å)	2.855(8)
		Cu1-O1 (Å)	2.322(5)
		N4-Cu1-N9 (°)	89.5(2)
		N1-Cu1-N5 (°)	88.9(2)
		N1-Cu1-N9 (°)	90.9(2)
		N1-Cu1-O1 (°)	90.9(2)
		N5-Cu1-O1 (°)	90.4(2)
		N9-Cu1-O1 (°)	93.3(2)
UdP-7		Cu1-N5 (bib-A) (Å)	2.014(2)
		Cu1-N4 (bib-B) (Å)	2.016(2)
		Cu1-N3 (bib-B) (Å)	2.757(2)
		N4-Cu1-N5 (°)	89.1(1)
		N4-Cu1-N3 (°)	89.4(2)
		N3-Cu1-N5 (°)	88.2(2)

Table S5. Dihedral angles between the imidazolyl and phenyl planes of the bib ligands, and corresponding torsional angles, for the four crystalline phases **UdP-7·2MeOHα**, **UdP-7·2MeOHβ**, **UdP-7·MeOH**, and **UdP-7**. Cu1 centers in **UdP-7·MeOH** and in **UdP-7** were depicted as octahedrons for sake of comparison.

Structures	Dihedral angles between imidazolyl planes and phenyl planes of ligands	Torsional angles
UdP-7·2MeOHα		  
UdP-7·2MeOHβ		 
UdP-7·MeOH		  
UdP-7		

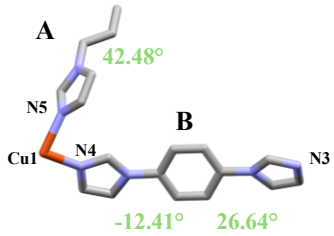
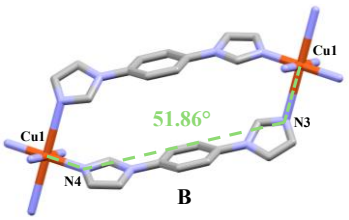
		

Table S6. Centroid-to-centroid distances between the aromatic planes of the bib ligands in the different **UdP-7** phases. Cu1 centers in **UdP-7·MeOH** and in **UdP-7** were depicted as octahedrons for sake of comparison.

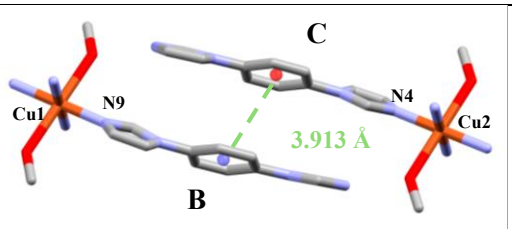
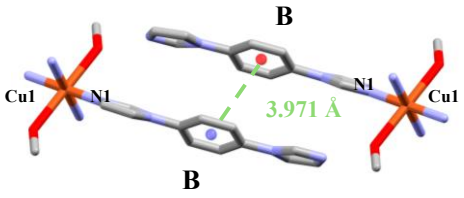
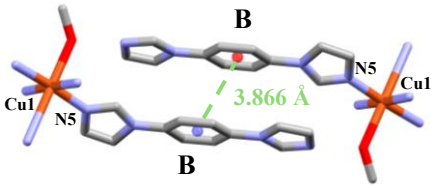
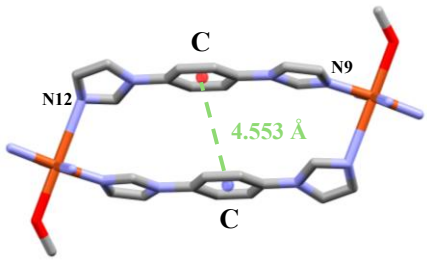
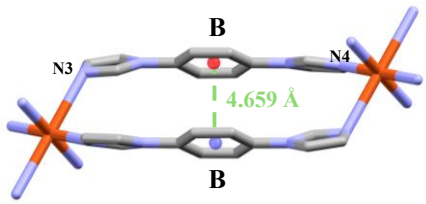
Structures	Centroids distances between bib planes
UdP-7·2MeOHα	
UdP-7·2MeOHβ	
UdP-7·MeOH	 
UdP-7	

Table S7. Top views of the Cu–bib square motifs in all **UdP-7** phases. Cu···Cu distances and internal angles (in yellow) are reported. A progressive shortening is observed along the bib-B (or bib-C) direction from **UdP-7·2MeOHβ** to **UdP-7**, consistent with the closer approach of the polymeric chains, while the bib-A distance, corresponding to the direction of polymer propagation, remains essentially unchanged. The small differences between **UdP-7·2MeOHα** and **UdP-7·2MeOHβ** can be attributed to the different experimental temperature (100 K and 200 K for the **α** and **β**, respectively). Hydrogen atoms and BF_4^- anions have been omitted for clarity. Cu1 centers in **UdP-7·MeOH** and in **UdP-7** were depicted as octahedrons for sake of comparison.

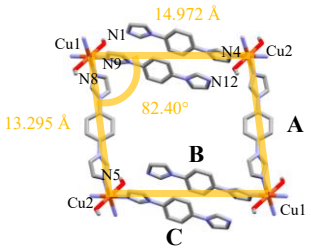
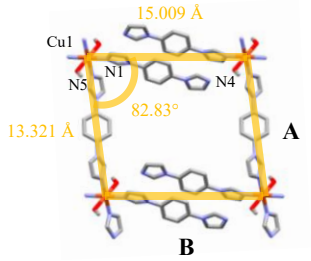
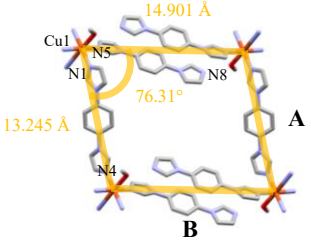
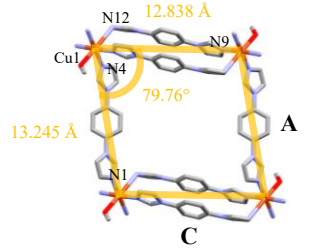
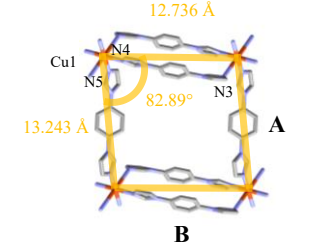
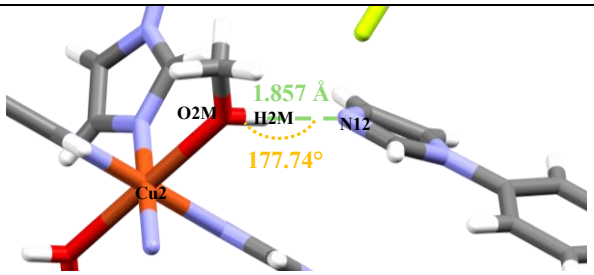
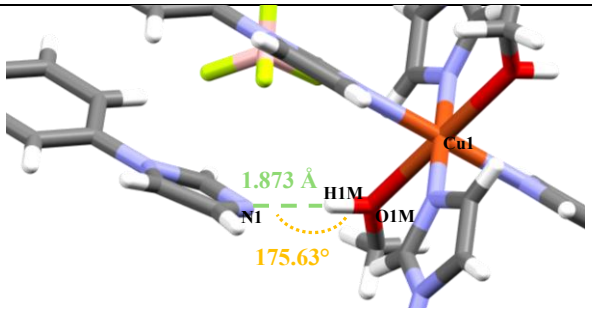
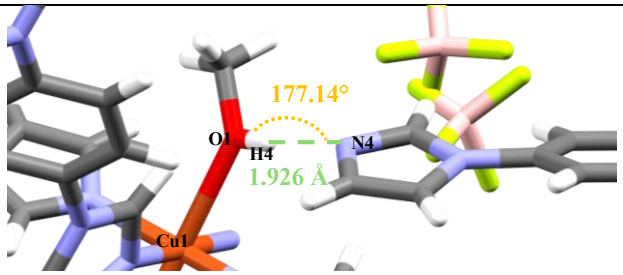
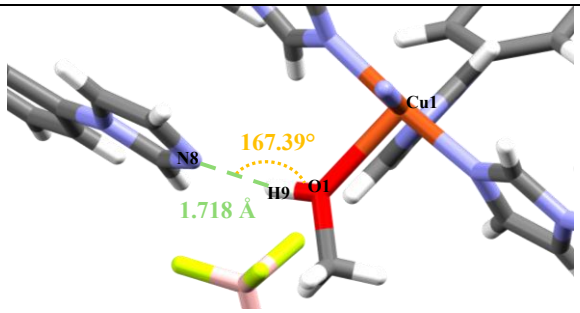
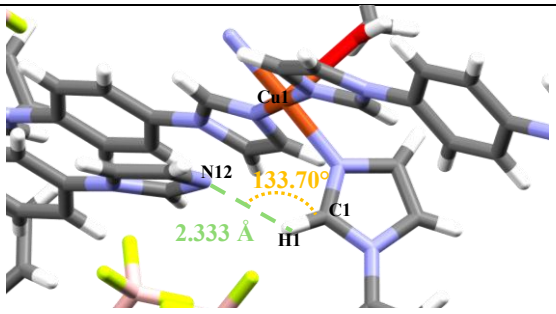
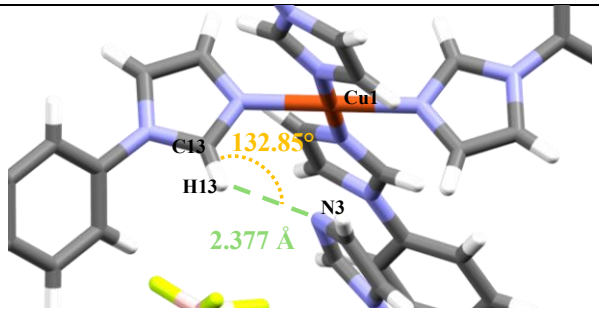
Structures	Views of the Cu-bib square motifs
UdP-7·2MeOHα	
UdP-7·2MeOHβ	
UdP-7·MeOH	 
UdP-7	

Table S8. Main hydrogen-bond-type interactions observed in **UdP-7·2MeOHα**, **UdP-7·2MeOHβ**, **UdP-7·MeOH**, and **UdP-7**. Distances refer to the H···A separation (Å), while angles correspond to the D–H···A geometry (°).

UdP-7·2MeOHα	
	
UdP-7·2MeOHβ	
UdP-7·MeOH	
	

UdP-7	

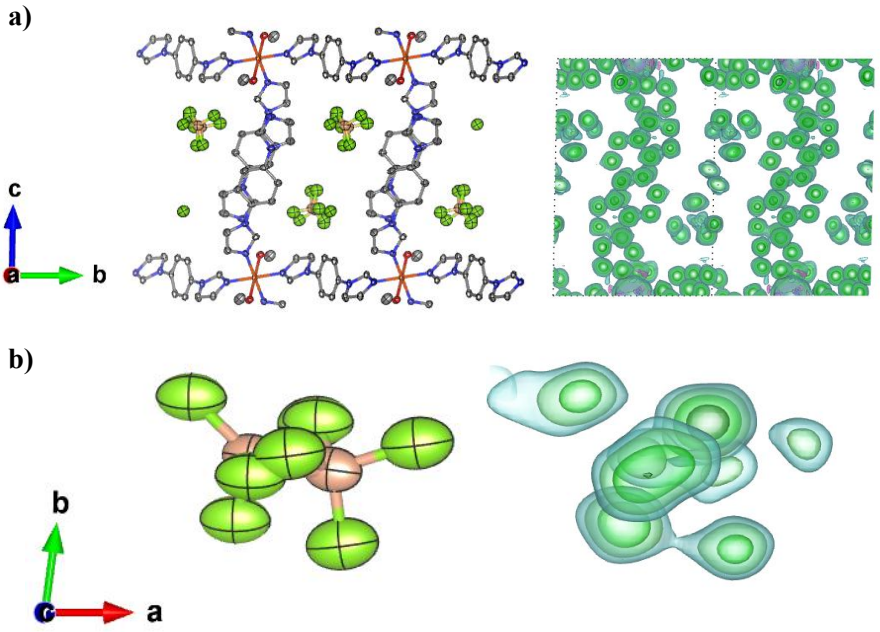


Figure S2. a) Electron density calculated from the observed structure factors (Fo) by Fourier synthesis (right), and modelled species (left). b) Modelled disordered structure of BF_4^- anions in the cavity (left) shown next to their underlying observed electron density (right). Four isosurface levels for the electron density were used, having respectively the following values of electrons/Å^3: 6 (dark green), 3.5 (light green), 2 (green-blue), 1.3 (light blue). Atom color: Cu orange; O red; N blue; B pink; F yellow; C grey; H white.[2]

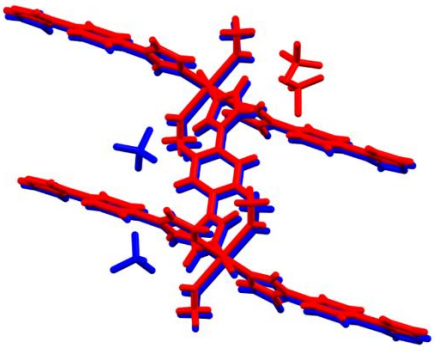


Figure S3. Structural overlap of **UdP-7·2MeOHα** (blue) and **UdP-7·2MeOHβ** (red) showing the nearly perfect superposition of the polymeric framework. Only the positions of the BF_4^- anions differ significantly due to their disordered nature in the β phase.

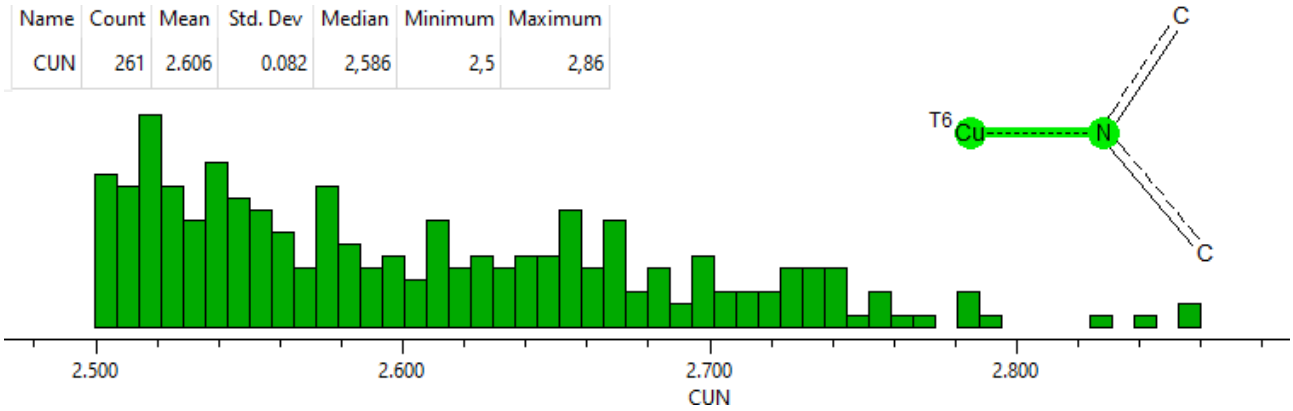
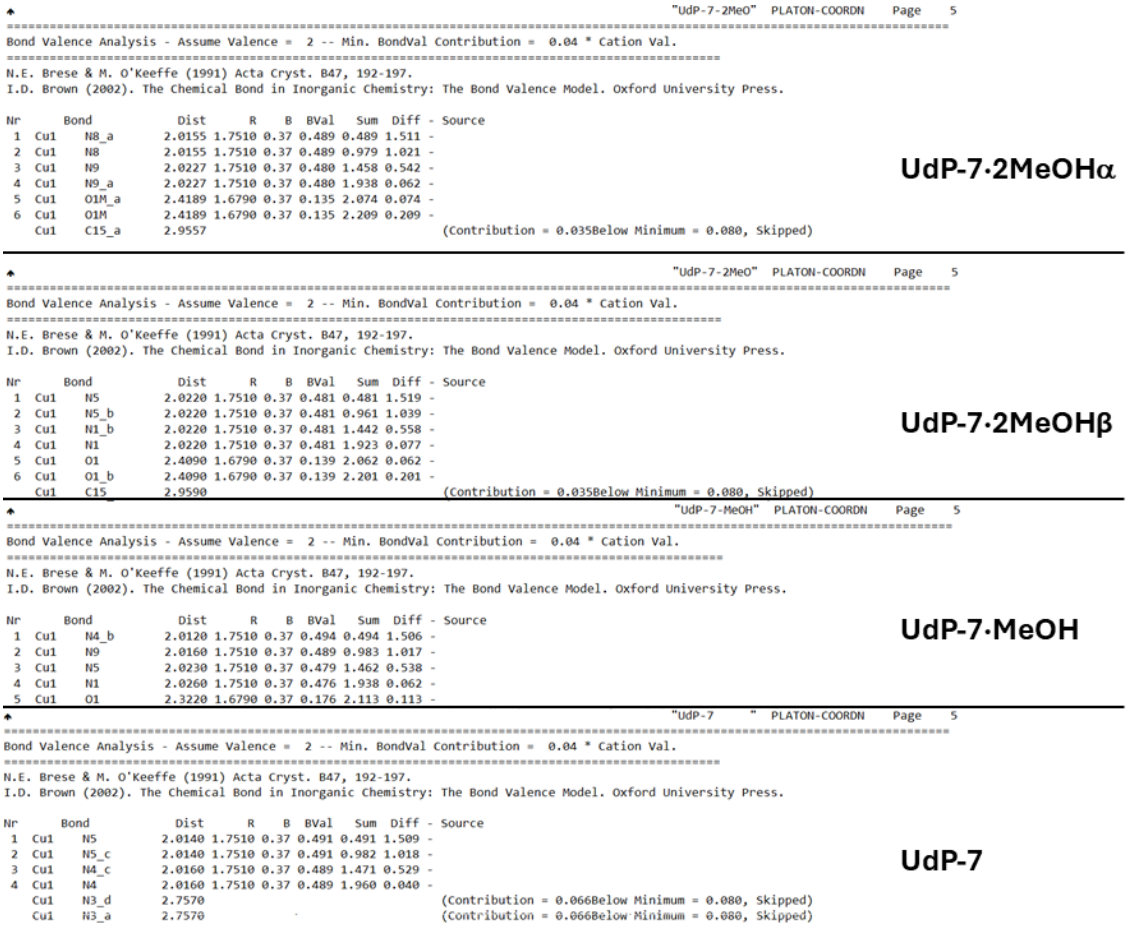


Figure S4. Analysis of the distribution of Cu–N bond lengths in the range 2.5–3.0 Å for the Cu-N(aromatic) systems shown in the figure, obtained by a CSD database search. The Cu-N bond was defined as unrestricted; Cu was settled as hexacoordinated and C-N-C moiety as delocalized. The search returned to 261 hits, with a median value of 2.586 Å and a range spanning from 2.50 Å to 2.86 Å.



"UdP-7-2MeO" PLATON-COORDN Page 5

Bond Valence Analysis - Assume Valence = 2 -- Min. BondVal Contribution = 0.04 * Cation Val.

N.E. Brese & M. O'Keeffe (1991) Acta Cryst. B47, 192-197.
I.D. Brown (2002). The Chemical Bond in Inorganic Chemistry: The Bond Valence Model. Oxford University Press.

Nr	Bond	Dist	R	B	BVal	Sum	Diff	Source
1	Cu1 N8_a	2.0155	1.7510	0.37	0.489	0.489	1.511	-
2	Cu1 N8	2.0155	1.7510	0.37	0.489	0.979	1.021	-
3	Cu1 N9	2.0227	1.7510	0.37	0.480	1.458	0.542	-
4	Cu1 N9_a	2.0227	1.7510	0.37	0.480	1.938	0.062	-
5	Cu1 O1M_a	2.4189	1.6790	0.37	0.135	2.074	0.074	-
6	Cu1 O1M	2.4189	1.6790	0.37	0.135	2.209	0.209	-
	Cu1 C15_a	2.9557						(Contribution = 0.035Below Minimum = 0.080, Skipped)

UdP-7·2MeOHα

"UdP-7-2MeO" PLATON-COORDN Page 5

Bond Valence Analysis - Assume Valence = 2 -- Min. BondVal Contribution = 0.04 * Cation Val.

N.E. Brese & M. O'Keeffe (1991) Acta Cryst. B47, 192-197.
I.D. Brown (2002). The Chemical Bond in Inorganic Chemistry: The Bond Valence Model. Oxford University Press.

Nr	Bond	Dist	R	B	BVal	Sum	Diff	Source
1	Cu1 N5	2.0220	1.7510	0.37	0.481	0.481	1.519	-
2	Cu1 N5_b	2.0220	1.7510	0.37	0.481	0.961	1.039	-
3	Cu1 N1_b	2.0220	1.7510	0.37	0.481	1.442	0.558	-
4	Cu1 N1	2.0220	1.7510	0.37	0.481	1.923	0.077	-
5	Cu1 O1	2.4090	1.6790	0.37	0.139	2.062	0.062	-
6	Cu1 O1_b	2.4090	1.6790	0.37	0.139	2.201	0.201	-
	Cu1 C15_	2.9590						(Contribution = 0.035Below Minimum = 0.080, Skipped)

UdP-7·2MeOHβ

"UdP-7-MeOH" PLATON-COORDN Page 5

Bond Valence Analysis - Assume Valence = 2 -- Min. BondVal Contribution = 0.04 * Cation Val.

N.E. Brese & M. O'Keeffe (1991) Acta Cryst. B47, 192-197.
I.D. Brown (2002). The Chemical Bond in Inorganic Chemistry: The Bond Valence Model. Oxford University Press.

Nr	Bond	Dist	R	B	BVal	Sum	Diff	Source
1	Cu1 N4_b	2.0120	1.7510	0.37	0.494	0.494	1.506	-
2	Cu1 N9	2.0160	1.7510	0.37	0.489	0.983	1.017	-
3	Cu1 N5	2.0230	1.7510	0.37	0.479	1.462	0.538	-
4	Cu1 N1	2.0260	1.7510	0.37	0.476	1.938	0.062	-
5	Cu1 O1	2.3220	1.6790	0.37	0.176	2.113	0.113	-

UdP-7·MeOH

"UdP-7 " PLATON-COORDN Page 5

Bond Valence Analysis - Assume Valence = 2 -- Min. BondVal Contribution = 0.04 * Cation Val.

N.E. Brese & M. O'Keeffe (1991) Acta Cryst. B47, 192-197.
I.D. Brown (2002). The Chemical Bond in Inorganic Chemistry: The Bond Valence Model. Oxford University Press.

Nr	Bond	Dist	R	B	BVal	Sum	Diff	Source
1	Cu1 N5	2.0140	1.7510	0.37	0.491	0.491	1.509	-
2	Cu1 N5_c	2.0140	1.7510	0.37	0.491	0.982	1.018	-
3	Cu1 N4_c	2.0160	1.7510	0.37	0.489	1.471	0.529	-
4	Cu1 N4	2.0160	1.7510	0.37	0.489	1.960	0.040	-
	Cu1 N3_d	2.7570						(Contribution = 0.066Below Minimum = 0.080, Skipped)
	Cu1 N3_a	2.7570						(Contribution = 0.066Below Minimum = 0.080, Skipped)

UdP-7

Figure S5. PLATON coordination analysis (CALC COORD) conducted on all the materials reported in this work.

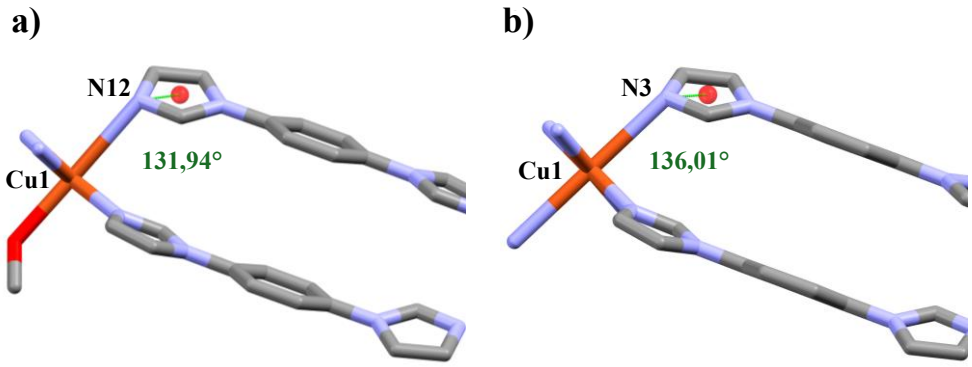


Figure S6. Representations of: (a) Cu1—N12 distance and "Cu1—N12" coordination angle (calculated considering the imidazole centroid) in **UdP-7·MeOH** and (b) Cu1—N3 distance and "Cu1—N3" coordination angle (calculated considering the imidazole centroid) in **UdP-7**.

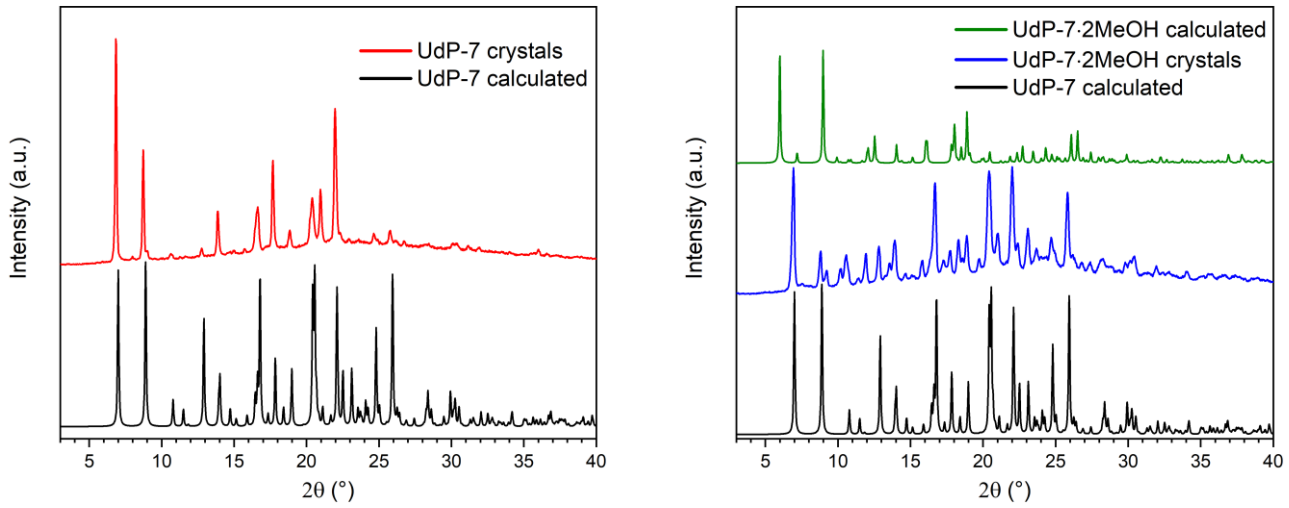


Figure S7. PXRD patterns comparison: (left) calculated **UdP-7** (black) and ground crystals of **UdP-7** (red); (right) calculated **UdP-7** (black), ground crystals of **UdP-7·2MeOH** (blue) and calculated **UdP-7·2MeOH** (green).

References

1 L. Link and R. Niewa, *J Appl Crystallogr*, 2023, **56**, 1855–1864.

2 C. Koschnick, M. W. Terban, R. Frison, M. Etter, F. A. Böhm, D. M. Proserpio, S. Krause, R. E. Dinnebier, S. Canossa and B. V. Lotsch, *J. Am. Chem. Soc.*, 2023, **145**, 10051–10060.