Electronic Supplementary Information (ESI)

Coordination Polymers with a Pyrazine-2,5-Diyldimethanol Linker: Supramolecular Networks through Hydrogen and Halogen Bonds

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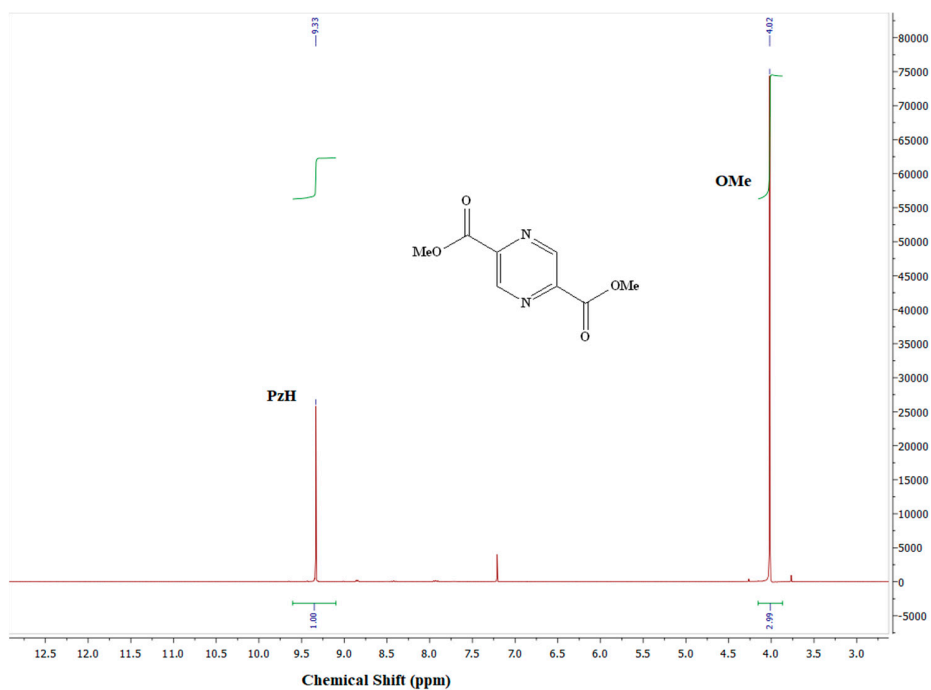[2] Bruker AXS GmbH Östliche, Rheinbrückenstraße 49, 76187 Karlsruhe, Germany; tobias.stuerzer@bruker.com

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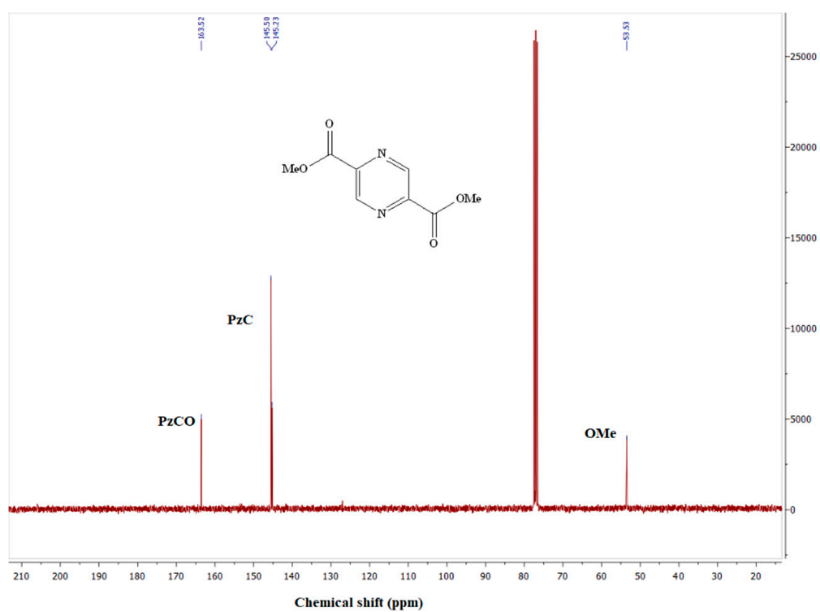
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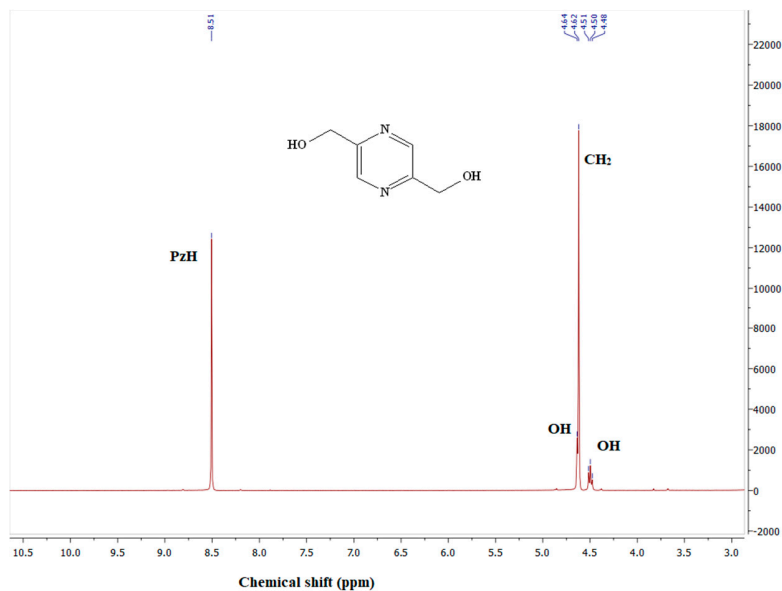
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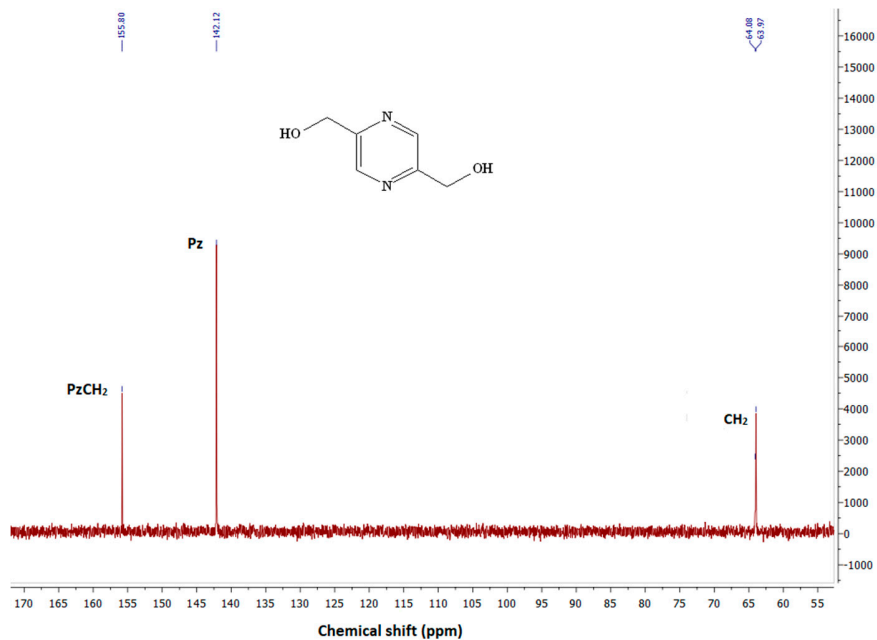
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Table S1. Crystallographic data and structure determination and refinement details for **pyzdmH2**, and **1–5**.

Compound	PyzdmH$_2$	1	2
Empirical formula	C$_6$H$_8$N$_2$O$_2$	C$_3$H$_8$Br$_2$CuNO$_3$	C$_6$H$_{12}$Cl$_4$N$_2$O$_4$Zn$_2$
Formula weight, fw	140.14	329.46	448.72
Temperature	296(2) K	140(2) K	143(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)
a	12.8997(8) Å	9.5705(4) Å	9.2773(4) Å
b	4.0557(3) Å	11.8961(4) Å	11.1104(4) Å
c	18.4031(12) Å	7.8107(3) Å	14.2326(6) Å
α	90°	90°	90°
β	100.550(3)°	112.729(2)°	104.728(2)°
γ	90°	90°	90°
Volume	946.52(11) Å^3	820.20(6) Å^3	1418.82(10) Å^3
Number of formula unit, Z	6	4	4
Density (calculated), D_c	1.475 Mg/m^3	2.668 Mg/m^3	2.101 Mg/m^3
Absorption coefficient, μ	0.113 mm^{-1}	12.356 mm^{-1}	4.138 mm^{-1}
F(000)	444	624	888
Crystal size	0.200 x 0.100 x 0.100 mm^3	0.100 x 0.100 x 0.100 mm^3	0.100 x 0.100 x 0.100 mm^3
Theta range for data collection	2.251 to 36.266°	2.307 to 38.357°	2.356 to 26.366°
Index ranges	-21<=h<=20, -5<=k<=6, -28<=l<=30	-16<=h<=15, -18<=k<=20, -11<=l<=13	-11<=h<=11, 0<=k<=13, 0<=l<=17
Reflections collected	13059	14181	2897
Independent reflections	3718 [R(int) = 0.0245]	4302 [R(int) = 0.0307]	2897 [R(int) = 0.065]
Completeness to theta = 25.242°	99.4 %	99.9 %	99.6 %
Absorption correction	Multi-scan / SABADS	Multi-scan / SABADS	Multi-scan / SABADS
Max. and min. transmission	0.7471 and 0.6836	0.7475 and 0.4787	0.7468 and 0.5519
Data / restraints / parameters	3718 / 0 / 145	4302 / 1 / 106	2897 / 4 / 181
Rint; Rσ	0.0245, 0.0272	0.0307, 0.0369	0.065, 0.0144
Goodness-of-fit on F2, GOF	1.057	1.018	1.125
Final R indices [I>2sigma(I)]	R1 = 0.0440, wR2 = 0.1222	R1 = 0.0268, wR2 = 0.0516	R1 = 0.0252, wR2 = 0.0656
R indices (all data)	R1 = 0.0581, wR2 = 0.1326	R1 = 0.0421, wR2 = 0.0554	R1 = 0.0273, wR2 = 0.0669
Largest diff. peak and hole	0.523 e.Å-3 at 0.75 Å from C8 and -0.227 e.Å-3 at 0.76 Å from C6	0.954 e.Å^{-3} at 0.73 Å from Br2 and -0.646 e.Å^{-3} at 0.80 Å from Cu	0.870 e.Å-3 at 0.05 Å from Zn1 and -0.388 e.Å-3 at 0.61 Å from C1
CCDC	2232274	2232622	2253333

$R_1 = \sum ||F_o| - |F_c|| - \sum |F_o|$; $wR_2 = [\sum w(F_o{}^2 - F_c{}^2)^2 - \sum w(F_o{}^2)^2]^{-1}$; GOF = $[\sum w(F_o{}^2 - F_c{}^2)^2 - (m - n)]^{-1}$; where m is the number of reflections and n is total number of parameters refined.

Table S1 Continued

Compound	3	4	5
Empirical formula	$C_6H_8Cl_4Hg_2N_2O_2$	$C_6H_{10}Cd_2Cl_4N_2O_3$	$C_6H_{10}Br_4Cd_2N_2O_3$
Formula weight, fw	683.12	524.76	702.60
Temperature	143(2) K	143(2)K	143(2)K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	*P*-1 (no. 2)	*C2/c* (no. 15)	*C2/c* (no. 15)
a	7.9304(3) Å	14.0241(6) Å	14.1197(7) Å
b	8.1346(3) Å	8.6911(3) Å	9.0025(5) Å
c	9.9597(4) Å	11.6961(5) Å	12.0247(6) Å
α	83.688(2)°	90°	90°
β	85.086(2)°	111.081(2)°	109.581(3)°
γ	78.472(2)°.	90°	90°
Volume	624.39(4) Å^3	1330.17(9) Å^3	1440.10(13) Å^3
Number of formula unit, Z	2	4	4
Density (calculated), D_c	3.633 Mg/m^3	2.620 Mg/m^3	3.241 Mg/m^3
Absorption coefficient, μ	25.398 mm^{-1}	3.995 mm^{-1}	14.047 mm^{-1}
F(000)	604	992	1280
Crystal size	0.200 x 0.100 x 0.100 mm3	0.200 x 0.100 x 0.100 mm^3	0.100 x 0.050 x 0.050 mm^3
Theta range for data collection	2.062 to 30.503°	2.814 to 26.369°	2.732 to 37.433°.
Index ranges	-11<=h<=11, -11<=k<=11, -14<=l<=14	-17<=h<=14, -10<=k<=9, -13<=l<=14	-23<=h<=17, -15<=k<=14, -14<=l<=20
Reflections collected	13598	6940	11176
Independent reflections	3811 [R(int) = 0.0332]	1365 [R(int) = 0.0186]	3296 [R(int) = 0.0529]
Completeness to theta = 25.242°	99.6 %	99.8 %	99.8 %
Absorption correction	Multi-scan / SABADS	Multi-scan / SABADS	Multi-scan / SABADS
Max. and min. transmission	0.7482 and 0.2147	0.7456 and 0.6016	0.7474 and 0.4955
Data / restraints / parameters	3811 / 2 / 151	1365 / 3 / 92	3296 / 5 / 92
Rint; Rσ	0.0332, 0.0285	0.0186, 0.0118	0.0529, 0.0615
Goodness-of-fit on F2, GOF	1.097	1.506	1.130
Final R indices [I>2sigma(I)]	R1 = 0.0229, wR2 = 0.0613	R1 = 0.0235, wR2 = 0.0667	R1 = 0.0443, wR2 = 0.0689
R indices (all data)	R1 = 0.0240, wR2 = 0.0620	R1 = 0.0236, wR2 = 0.0667	R1 = 0.0634, wR2 = 0.0742
Largest diff. peak and hole	3.041 e.Å^{-3} at 0.76 Å from Hg2 and -3.229 e.Å^{-3} at 0.76 Å from Hg1	0.591 e.Å^{-3} at 0.91 Å from C3 and -1.032 e.Å^{-3} at 0.84 Å from Cl1	1.79 e.Å^{-3} at 1.80 Å from Br1 and -1.35 e.Å^{-3} at 2.09 Å from C2
CCDC	2236315	2249852	2236379

$R_1 = \sum||F_o| - |F_c||-\sum|F_o|$; $wR_2 = [\sum w(F_o{}^2 - F_c{}^2)^2-\sum w(F_o{}^2)^2]^{-1}$; GOF = $[\sum w(F_o{}^2 - F_c{}^2)^2 -(m - n)]^{-1}$; where m is the number of reflections and n is total number of parameters refined.

Table S2. Selected bond lengths [Å], angles and torsion angles [°] for **pyzdmH2** and **1–5** with standard uncertainties in parentheses.

PyzdmH2					
Bond lengths [Å]		**Angles [°]**		**Torsion angles [°]**	
O(1)-C(1)	1.4154(14)	C(1)-O(1)-H(1)	109.2(10)	H(1)-O(1)-C(1)-C(2)	134.76
O(1)-H(1)	0.871(16)	C(4)-O(2)-H(2)	107.7(11)	H(1)#i-O(1)#i-C(1)#i-C(2)#i	-134.76
O(2)-C(4)	1.4136(13)	C(9)-O(3)-H(3)	109.0(11)	H(2)-O(2)-C(4)-C(5)	155.28
O(2)-H(2)	0.853(16)	O(1)-C(1)-C(2)	110.65(8)	H(3)-O(3)-C(9)-C(8)	78.82
O(3)-C(9)	1.4225(12)	O(2)-C(4)-C(5)	109.85(8)	O(1)-C(1)-C(2)-N(1)	166.529(89)
O(3)-H(3)	0.852(16)	O(3)-C(9)-C(8)	111.74(7)	O(2)-C(4)-C(5)-N(2)	171.203(82)
				O(3)-C(9)-C(8)-N(3)	-67.456(109)

Symmetry transformations used to generate equivalent atoms: i = 1–x, 1–y, –z, ii = 2-x, 2-y, 1-z, iii = x, 3/2-y, -1/2+z, iv = x, -1+y, z, v = x, 1+y, z, vi = 1-x, -1/2+y, 1/2-z.

1					
Cu-O(1)	1.9968(12)	O(1)-Cu-N(1)	79.98(5)	H(1)-O(1)-C(1)-C(2)	147.02
Cu-N(1)	2.0281(13)	Br(2)-Cu-Br(1)	95.318(9)	Cu-O(1)-C(1)-C(2)	17.13(17)
Cu-Br(1)	2.4112(3)	O(1)-Cu-O(2)	85.09(5)	Cu-N(1)-C(2)-C(1)	6.36(18)
Cu-Br(2)	2.3627(3)	C(1)-O(1)-Cu	117.32(10)	O(1)-C(1)-C(2)-N(1)	-14.9(2)
Cu-O(2)	2.6590(15)	C(2)-N(1)-Cu	114.65(10)	C(3)-N(1)-C(2)-C(3)#i	1.0(3)
Cu-Br(1)#ii	**3.0672(3)**	C(1)-O(1)-H(1)	110.9(16)		
O(1)-C(1)	1.4251(19)	O(1)-C(1)-C(2)	107.93(13)		
O(1)-H(1)	0.82(16)	H(2A)-O(2)-H(2B)	106(2)		
O(2)-H(2A)	0.82(2)	H(3A)-O(3)-H(3B)	108(2)		
O(2)-H(2B)	0.78(2)	Cu-O(1)-H(1)	111.6(15)		
O(3)-H(3A)	0.87(2)	Cu-O(2)-H(2A)	99.7(16)		
O(3)-H(3B)	0.80(2)	Cu-O(2)-H(2B)	105.9(17)		

Symmetry transformations used to generate equivalent atoms: Symmetry transformations used to generate equivalent atoms: i = 2-x, 1-y, 2-z, ii = 2-x, 1-y, 1-z, iii = 1-x, 1-y, 1-z, iv = 1-x, -1/2+y, 1/2-z, v = 1-x, 1/2+y, 1/2-z, vi = 1-x, 1-y, -z, vii = 2-x, -1/2+y, 3/2-z, viii = x, 1/2-y, -1/2+z, ix = x, y, z-1, x = x, y, z+1.

2					
Zn(2)-Cl(3)	2.2529(6)	O(1)-Zn(1)-N(1)	75.53(7)	Zn(1)-O(1)-C(1)-C(3)	37.4(2)
Zn(2)-Cl(4)	2.2531(6)	O(2)-Zn(1)-N(2)	74.94(7)	Zn(1)-O(2)-C(2)-C(5)	-11.0(3)
Zn(2)-Cl(2)	2.2773(6)	N(1)-Zn(1)-N(2)	101.54(8)	C(5)-N(2)-C(6)-C(5)#ii	1.0(4)
Zn(2)-Cl(1)	2.3115(6)	O(3)-Zn(1)-O(1)	84.07(7)	C(3)-N(1)-C(4)-C(3)#i	1.3(4)
Zn(1)-Cl(1)	2.4669(6)	O(3)-Zn(1)-N(2)	98.20(7)	O(1)-C(1)-C(3)-N(1)	-26.5(3)
Zn(1)-O(3)	**2.0447(18)**	C(1)-O(1)-Zn(1)	114.78(14)	N(2)-C(5)-C(2)-O(2)	6.9(3)
Zn(1)-N(1)	2.112(2)	C(2)-O(2)-Zn(1)	120.35(14)	O(1)-C(1)-C(3)-C(4)#i	155.1(2)
Zn(1)-O(1)	2.0972(17)	C(1)-O(1)-H(1)	110(2)	Zn(1)-N(1)-C(3)-C(1)	4.1(3)
Zn(1)-O(2)	2.1259(18)	C(2)-O(2)-H(2)	107(2)	Zn(1)-N(2)-C(5)-C(2)	-0.1(3)
Zn(1)-N(2)	2.1451(19)	O(2)-Zn(1)-Cl(1)	171.37(5)	H(1)-O(1)-C(1)-C(3)	175.52
O(1)-C(1)	1.416(3)	Zn(2)-Cl(1)-Zn(1)	122.75(3)	H(2)-O(2)-C(2)-C(5)	176.68
O(2)-C(2)	1.404(3)	Zn(1)-O(1)-H(1)	120(2)		
O(1)-H(1)	0.871(18)	Zn(1)-O(2)-H(2)	131(2)		
O(2)-H(2)	0.835(18)	H(3A)-O(3)-H(3B)	107(3)		
O(3)-H(3A)	0.81(4)	H(4A)-O(4)-H(4B)	111(4)		
O(3)-H(3B)	0.82(4)	Zn(1)-O(3)-H(3A)	128(2)		
O(4)-H(4A)	0.853(19)	Zn(1)-O(3)-H(3B)	121(2)		
O(4)-H(4B)	0.848(18)	Cl(3)-Zn(2)-Cl(4)	110.74(2)		
		Cl(3)-Zn(2)-Cl(2)	112.28(2)		
		Cl(4)-Zn(2)-Cl(2)	109.72(2)		
		Cl(3)-Zn(2)-Cl(1)	105.95(2)		
		Cl(4)-Zn(2)-Cl(1)	110.59(2)		
		Cl(2)-Zn(2)-Cl(1)	107.45(2)		

Symmetry transformations used to generate equivalent atoms: i = 1-x, 1-y, 1-z, ii = 1-x, 2-y, 1-z, iii = -1+x, y, iii = x-1, y, z, iv = x-1/2, -y+3/2, z+1/2, v = -x+1/2, y+1/2, -z+1/2, vi = -x+1/2, y-1/2, -z+1/2, vii = x-1/2, -y+3/2, z-1/2, viii = x+1/2, -y+3/2, z+1/2, ix = x+1/2, -y+3/2, z-1/2.

Table S2 Continued

3					
Bond lengths [Å]		**Angles [°]**		**Torsion angles [°]**	
Hg(1)-Cl(1)	2.3491(9)	N(1)-Hg(1)-O(1)	63.63(8)	H(1)-O(1)-C(1)-C(2)	104.65(3)
Hg(1)-Cl(2)	2.3558(8)	Cl(1)-Hg(1)-Cl(2)	163.73(3)	N(1)-C(2)-C(1)-O(1)	27.44(3)
Hg(1)-N(1)	2.575(3)	Cl(1)-Hg(1)-O(1)	111.59(6)	H(2)-O(2)-C(6)-C(5)	-176.93(3)
Hg(1)-O(1)	2.642(3)	Cl(1)-Hg(2)-Cl(2)	176.69 (3)	O(2)-C(6)-C(5)-N(2)	43.03(3)
Hg(2)-N(2)	2.710(3)	Cl(4)-Hg(2)-Cl(3)	165.83(3)	N(1)-C(2)-C(3)-N(2)	1.18(3)
Hg(2)-Cl(4)	2.3104(8)	Hg(1)-O(1)-H(1)	112(4)	N(1)-C(4)-C(5)-N(2)	0.84(3)
Hg(2)-Cl(3)	2.3182(9)	Cl(2)-Hg(1)-N(1)	103.61(7)	H(2)-O(2)-C(6)-C(5)	-176.93(3)
Hg(2)-Cl(1)#i	**3.0705(10)**	Cl(4)-Hg(2)-N(2)	109.25(7)	Hg(1)-O(1)-C(1)-C(2)	-27.49(3)
Hg(2)-Cl(2)#i	**3.0502(10)**	C(6)-O(2)-H(2)	109(4)	Hg(1)-N(1)-C(2)-C(1)	-14.11(4)
O(1)-H(1)	0.822(19)	C(1)-O(1)-H(1)	112(4)		
O(2)-H(2)	0.830(19)				
O(1)-C(1)	1.420(4)				
O(2)-C(6)	1.416(4)				
Symmetry transformations used to generate equivalent atoms: i = 2-x, 1-y, 1-z, ii = -x+1,-y+1,-z+1, iii = x, y+1/2, z-1, iv = -x+1, 2-y,-z+1, v = x, -1+y, 1+z, vi = 2-x, -y, 1-z, vii = x, 1+y, z-1, viii = 2-x, 2-y, -z, ix = x, y, 1+z.					

4					
Cd-N(1)	2.367(4)	N(1)-Cd-O(1)	69.36(13)	H(1A)-O(1)-Cd-N(1)	135.2(6)
Cd-O(1)	2.418(3)	N(1)-Cd-Cl(2)	92.98(10)	H(1B)-O(1)-Cd-N(1)	-96.7(8)
Cd-Cl(1)	2.5719(11)	O(1)-Cd-Cl(2)	162.18(8)	H(1A)-O(1)-C(1)-C(2)	140.4(6)
Cd-Cl(2)	2.5582(12)	N(1)-Cd-Cl(1)	157.29(10)	H(1B)-O(1)-C(1)-C(2)	73.7(8)
Cd-Cl(1)#i	2.6055(12)	O(1)-Cd-Cl(1)	88.74(8)	Cd-N(1)-C(2)-C(3)#iii	164.7(4)
Cd-Cl(2)#ii	2.6752(12)	Cl(2)-Cd-Cl(1)	109.07(4)	Cd-O(1)-C(1)-C(2)	-36.9(5)
O(1)-H(1B)	0.85(2)	O(1)-Cd-Cl(1)#i	81.56(9)	N(1)-C(2)-C(1)-O(1)	35.4(6)
O(1)-H(1A)	0.85(2)	Cl(2)-Cd-Cl(1)#i	99.23(4)	Cd-N(1)-C(2)-C(1)	-16.1(5)
O(2)-H(2A)	0.8012	Cl(1)#i-Cd-Cl(2)#ii	173.47(4)	C(3)-N(1)-C(2)-C(3)#iii	-1.7(7)
O(2)-H(2B)	0.9293	Cd-Cl(1)-Cd#i	90.96(4)	Cd-Cl(1)-Cd#i-Cl(1)#i	-23.1(5)
		Cd-Cl(2)-Cd#ii	94.51(4)	Cd-Cl(2)-Cd#ii-Cl(2)#ii	0.00(4)
		Cd-O(1)-H(1B)	98(10)		
		Cd-O(1)-H(1A)	94(9)		
		H(2A)-O(2)-H(2B)	104.2		
Symmetry transformations used to generate equivalent atoms: i = -x+1,y ,-z+1/2, ii = -x+1,-y+1,-z+1, iii = -x+1/2,-y+1/2,-z+1, iv = -x+1,-y,-z+1, v = x, 1-y, 1/2+z, vi = x, -y, 1/2+z, vii = x, -1+y, z, viii = x-1/2, y-1/2, z, ix = x, y+1, z, x = x, -y, z-1/2, xi = x+1/2, y+1/2, z.					

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Cd-N(1)	2.377(4)	N(1)-Cd-O(1)	69.11(12)	H(1)-O(1)-C(1)-C(2)	-152.7(6)
Cd-O(1)	2.455(3)	N(1)-Cd-Br(2)	93.46(10)	H(1)-O(1)-Cd-N(1)	140.8(6)
Cd-Br(1)	2.6961(5)	O(1)-Cd-Br(2)	162.24(7)	Cd-O(1)-C(1)-C(2)	-37.3(4)
Cd-Br(2)	2.6868(6)	N(1)-Cd-Br(1)	156.40(10)	Cd-N(1)-C(2)-C(3)#iii	167.5(4)
Cd-Br(1)#i	2.7477(6)	O(1)-Cd-Br(1)	87.98(7)	Cd-N(1)-C(2)-C(1)	-14.6(6)
Cd-Br(2)#ii	2.8068(6)	Br(2)-Cd-Br(1)	109.70(18)	C(3)-N(1)-C(2)-C(3)#iii	-0.4(8)
O(1)-H(1A)	0.851(10)	O(1)-Cd-Br(1)#i	81.40(8)	O(1)-C(1)-C(2)-N(1)	35.2(6)
O(1)-H(1B)	0.850(10)	Br(2)-Cd-Br(1)#i	97.428(18)	Cd-Br(1)-Cd#i-Br(1)#i	-24.4(16)
O(2)-H(2A)	0.8399	Br(1)#i-Cd-Br(2)#ii	174.47(19)	Cd-Br(2)-Cd#ii-Br(2)#ii	0.0(18)
O(2)-H(2B)	0.7237	Cd-Br(1)-Cd#i	88.48(16)		
		Cd-Br(2)-Cd#ii	92.33(17)		
		Cd-O(1)-H(1A)	105(7)		
		H(2A)-O(2)-H(2B)	105.5		
Symmetry transformations used to generate equivalent atoms: i = -x+1, y,-z+3/2, ii = -x+1,-y+1,-z+1, iii = -x+3/2,-y+1/2,-z+1, iv = x,-y+1, z, v = x, y+1, z, vi = 1-x, y+1, 3/2-z, vii = 1-x, y-1, 3/2-z, viii = -x+1, 3-y, 1-z, ix = -x+1, -y, 1-z, x = x+1/2, -1/2+y, z.					

X-ray Crystallography of pyzdmH2

The colorless crystals of pyrazine-2,5-diyldimethanol (pyzdmH2) grew in water and analyzed by single-crystal X-ray diffraction. The diffraction pattern shows reflections with weak intensities especially in the high angle region. XPREP suggested a primitive monoclinic unit cell as the higher metric symmetry with R_{sym} of 1.9%. Analysis of systematic absences with respect to the value of $|E2–1| = 1.037$ lead to an acceptable centrosymmetric space group $P2_1/c$ (no.14) with R_{int} of 2.4 % and R_σ of 2.7 %. Completion of the structural model including to assign the positions of the hydrogen atoms of the hydroxyl groups of pyzdmH2 were done without using restrains and constrains. The structure refinement converged to a final value of $R1$ 4.40 % and $wR2$ 1.33%. The X-ray diffraction experiment and structure determination details are summarized in Table S1.

Table S3. Hydrogen bond interactions for pyzdmH2 [Å and °] with standard uncertainties in parentheses.

D-H⋯A	d(D-H)	d(H⋯A)	d(D⋯A)	<(DHA)
O(1)-H(1)⋯N(2)	0.87(16)	1.97(16)	2.84(12)	171
O(2)-H(2)⋯O(3)#iii	0.85(16)	1.87(16)	2.72(11)	174
O(3)-H(3)⋯N(3)#ii	0.85(16)	1.99(16)	2.80(11)	160
C(1)-H(1A)⋯O(1)#v	0.97	2.42(8)	3.39(3)	174
C(4)-H(4B)⋯O(2)#iv	0.97	2.44(8)	3.36(15)	159
C(9)-H(9A)⋯O(3)#v	0.97	2.59(8)	3.49(15)	154
Intra C(3)-H(3A)⋯O(1)#i	0.93	2.43(16)	2.78(13)	102
Intra C(6)-H(6)⋯O(2)	0.93	2.40(7)	2.74(12)	102

Symmetry transformations used to generate equivalent atoms: i = 1-x, 1-y, -z #ii = -x+2, -y+2, -z+1 #iii = x, -y+3/2, z-1/2 #iv = x, -1+y, z #v = x, 1+y, z.

Table S4. Analysis of ring-interactions Cg(I)-Cg(J) for pyzdmH2 with standard uncertainties in parentheses.

Cg(I)⋯Cg(J)	d(Cg(I)⋯Cg(J))	Alpha	Slippage
Cg(1)⋯Cg(1)#v	4.0557(7)	0.02(5)	2.078
Cg(1)⋯Cg(1)#iv	4.0558(7)	0.02(5)	2.078
Cg(2)⋯Cg(2)#iv	4.0557(6)	0.00(5)	2.168
Cg(2)⋯Cg(2)#v	4.0557(6)	0.00(5)	2.168

Symmetry transformations used to generate equivalent atoms: iv = x, -1+y, z and v = x, 1+y, z, Cg(1) = N1-C2-C3^i-N1^i-C2^i-C3, and Cg(2) = N2-C5-C6-N3-C8-C7. Cg-Cg Distance between ring centroids (Å), Alpha = Dihedral angle between planes I and J (°), Slippage = Distance between Cg(I) and perpendicular projection of Cg(J) on ring I (Å). The pyrazine rings are essentially flat in the both conformations with r.m.s. deviation for Cg(1) = 0.001 Å, Cg(2) = 0.005 Å respectively.
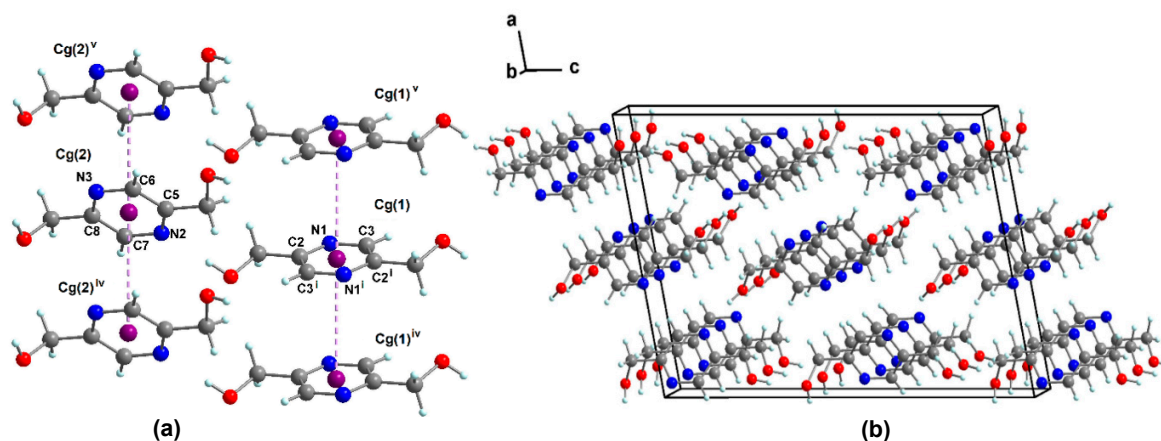
Figure S5. (a) π-π interactions between the pyrazine rings are depicted by the dashed bonds in light purple color. **(b)** A view of the cell packing diagram of pyzdmH2.

X-ray Crystallography of $\{[Cu(pyzdmH_2)_{0.5}(\mu\text{-Br})(Br)(H_2O)] \cdot H_2O\}_n$ (1)

Greenish colored block crystals of **1** grew in water and analyzed by single-crystal X-ray diffraction. The diffraction pattern was almost completely indexed using APEX4 using an orientation matrix and reciprocal lattice of the crystal showed an entirely single phase with a point group $2/m$ symmetry. The higher metric symmetry suggested by XPREP was a primitive monoclinic unit cell which has R_{sym} of 2.2 %. Analysis of systematic absences with respect to the value of $|E2–1| = 0.952$ lead to an acceptable monoclinic space group $P2_1/c$ (no.14) with R_{int} of 3.02 % and R_σ of 3.69 %. The O1-H1 bond distance in pyzdmH2 geometrically restrained to 0.85 Å (DFIX 0.85 O1 H1). The structure refinement converged to a final value of $R1 = 2.68$ % and $wR2 = 5.5\%$. The X-ray diffraction experiment and structure determination details are summarized in Table S1.

Table S5. Hydrogen bond interactions for **1** [Å and °] with standard uncertainties in parentheses.

| D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
O(1)-H(1)···O(2)#iii	0.82	1.82(2)	2.63(18)	172
O(2)-H(2A)···O(3)#iv	0.82	1.96(2)	2.77(21)	172.86
O(2)-H(2B)···O(3)#iii	0.78	2.06(2)	2.83(20)	169
O(3)-H(3A)···Br(1)#v	0.87	2.55(2)	3.22(16)	135.3
O(3)-H(3B)···Br(2)#vi	0.80	2.49(2)	3.29(15)	178
C(1)-H(1B)#vii···Br(1)	0.99	3.23(2)	3.94(17)	130
O(3)-H(3A)#vi···Br(1)	0.87	3.21(2)	3.68(13)	116
C(3)-H(3)#viii···Br(1)	0.95	3.24(2)	3.47(16)	96
O(2)-H(2B)#iii···Br(2)	0.78	3.11(2)	3.49(17)	113
O(3)-H(3B)···Br(2)	0.80	3.10(2)	3.36(14)	102
C(1)-H(1A)···Br(2)#x	0.99	3.13(2)	3.82(19)	128
C(1)-H(1A)···Br(2)#iii	0.99	3.09(2)	4.03(19)	159
Intra C(3)-H3···Br(1)	0.95	2.76(2)	2.37(15)	123
Intra C(3)-H3#ii···Br(2)	0.95	3.03(2)	3.48(19)	110
Intra O(1)-H1···Br(2)	0.82	2.90(2)	3.04(13)	93

Symmetry transformations used to generate equivalent atoms: i = 2-x, 1-y, 2-z, ii = 2-x, 1-y, 1-z, iii = 1-x, 1-y, 1-z, iv = 1-x, -1/2+y, 1/2-z, v = 1-x, 1/2+y, 1/2-z, vi = 1-x, 1-y, -z, vii = 2-x, -1/2+y, 3/2-z, viii = x, 1/2-y, -1/2+z, ix = x, y, z-1, x = x, y, z+1.

Table S6. Analysis of ring-interactions O-H···Cg(chelate-ring) for **1** with standard uncertainties in parentheses.

X-H···Cg	d(H···Cg)	<(X-H···Cg)
O(2)-H(2B)···Cg(2)	2.93(2)	89.9(19)

Cg(2) = Cu-O1-C1-C2-N1.

Table S7. Short halogen bond interactions for **1** with standard uncertainties in parentheses.

I···J	d(I···J)	<(X-I···J)
Br(1)···O(3)#iv	3.2247(16)	Cu 89.815(5)
Br(2)···O(3)	3.3620(16)	Cu 131.48(3)
O(2)···Br(2)#iii	3.4850(16)	Cu 120.28(5)

Symmetry transformations used to generate equivalent atoms: i = 2-x, 1-y, 2-z, ii = 2-x, 1-y, 1-z, iii = 1-x, 1-y, 1-z, iv = 1-x, -1/2+y, 1/2-z, v = 1-x, 1/2+y, 1/2-z, vi = 1-x, 1-y, -z, vii = 2-x, -1/2+y, 3/2-z, viii = x, 1/2-y, -1/2+z, ix = x, y, z-1, x = x, y, z+1.

X-ray Crystallography of $\{[Zn_2(pyzdmH2)(\mu\text{-}Cl)(Cl)_3(H_2O)] \cdot H_2O\}_n$ (2)

Colorless block crystals of **2** grew in water and analyzed by single-crystal X-ray diffraction. The images showed many reflection spots which are closed to each other without an obvious periodicity. By looking closer to the reciprocal lattice from the whole dataset, it was obviously recognized two domains (two diffraction patterns) that rotated to each other about -180 ° around vector 1 0 0 (Figure S6, a non-merohedral twin crystal). The two domains have been separately indexed, the unit-cell constants and the orientation matrices were determined by using APEX4. The data reduction and scaling to generate HKLF 4 (the merging has been done by APEX 4, R_{int} = 6.5%, twin fraction ratio = 1.58) and HKLF 5 (using the domain 1 depicted by the gray spots in Figure S6) worked without any issues. By using HKLF 4, the higher metric symmetric suggested by XPREP was compatible with a primitive monoclinic unit cell. Analysis of systematic absences with respect to the value of |E2–1| = 0.990 lead to an acceptable monoclinic space group $P2_1/n$ (no.14) with R_σ of 1.4 %. The structure was successfully solved and refined by using HKLF 4 with lower R-values ($R1$ = 2.5 % and $wR2$ = 8.5%) than using HKLF 5 ($R1$ = 3.75 % and $wR2$ = 11.15%.). Hydrogen atoms attached to the two oxygen atoms (O1-H1 and O2-H2) from the hydroxyl groups in **pyzdmH2** and coordinated and non-coordinated water molecule hydrogens (O3-H3A, O3-H3B, O4-H4A and O4-H4B) were all founded from Fourier difference maps and refined freely with U iso (H) = 1.5U eq (O). The O1-H1, O2-H2, O4-H4A and O4-H4B bond distances all geometrically restrained to 0.85 Å (DFIX 0.85 O1 H1, DFIX 0.85 O2 H2, DFIX 0.85 O4 H4A, DFIX 0.85 O4 H4B). The X-ray diffraction experiment and structure determination details are summarized in Table S1.
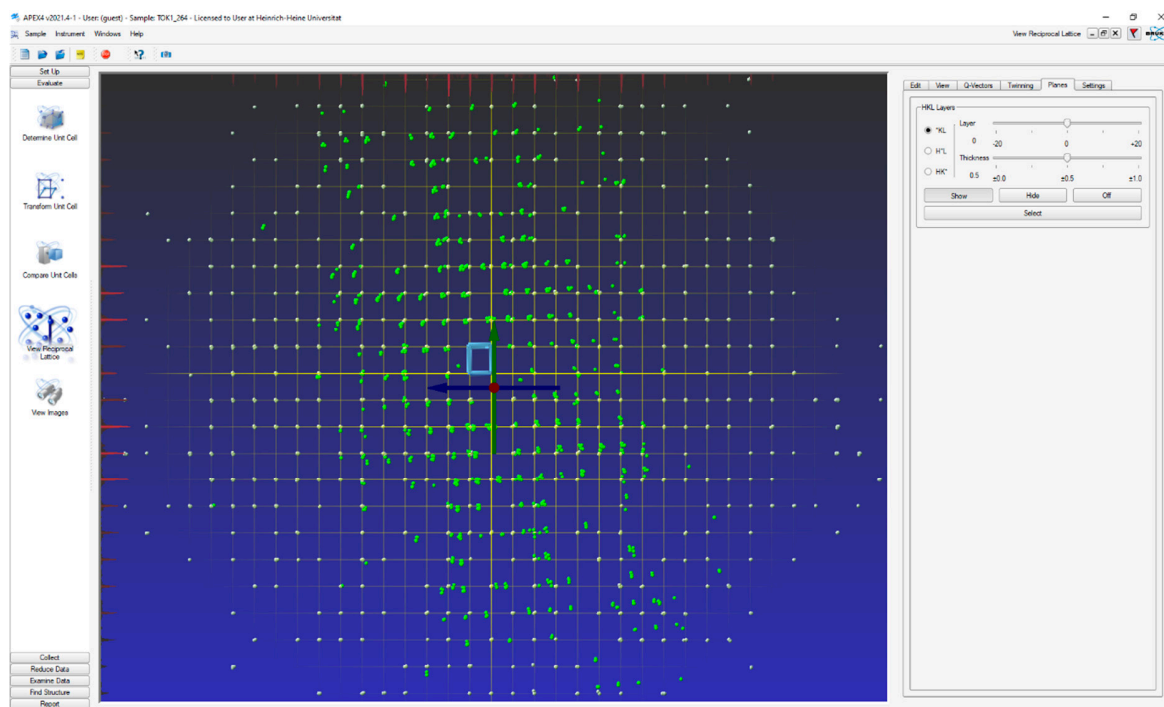
Figure S6. Reciprocal lattice plot of the H = 0 layer of the non-merohedral twin crystal **2** showing the two domains in gray (domain 1) and green (domain 2) colors.

Table S8. Hydrogen bond interactions for **2** [Å and °] with standard uncertainties in parentheses.

D-H⋯A	d(D-H)	d(H⋯A)	d(D⋯A)	<(DHA)
O(1)-H(1)⋯O4#iii	0.87(2)	1.72(2)	2.59(3)	**175**
O(2)-H(2)⋯Cl2#iv	0.83(3)	2.25(3)	3.08(19)	176
O(3)-H(3B)⋯Cl3#iv	0.82(4)	2.38(4)	3.16(2)	160
O(3)-H(3A)⋯Cl4#v	0.82(4)	2.29(4)	3.10(2)	**170**
O(4)-H(4A)⋯Cl4	0.85(3)	2.38(3)	3.16(2)	153
O(4)-H(4B)⋯Cl2	0.84(3)	2.55(4)	3.29(2)	148
C(1)-H(1B)⋯O4#i	0.990	2.60(4)	3.27(2)	125
O(4)-H(4B)#iii⋯O3	0.84(3)	2.87(4)	3.19(2)	104
C(4)-H(4)#vii⋯Cl3	0.990	2.83(4)	3.72(2)	156
C(2)-H(2A)#ix⋯O4	0.990	2.87(4)	3.412)	63
C(2)-H(2A)⋯Cl1#viii	0.990	2.99(4)	3.82(2)	142
C(1)-H(1B)#v⋯Cl3	0.990	3.03(4)	3.85(2)	141
Intra O(1)-(H1)⋯O3	0.87(2)	2.68(3)	2.772)	87
Intra O(3)-H(3B)⋯O2	0.82(4)	2.88(4)	2.96(2)	76
Intra C(2)-H(2B)#ii⋯Cl2	0.990	3.15(4)	3.79(2)	124
Intra C(6)-H(6)⋯Cl1	0.950	2.86(4)	3.49(2)	125
Intra C(6)-H(6)⋯Cl2	0.950	2.77(4)	3.51(2)	135

Symmetry transformations used to generate equivalent atoms: i = 1-x, 1-y, 1-z, ii = 1-x, 2-y, 1-z, iii = x-1, y, z, iv = x-1/2, -y+3/2, z+1/2, v = -x+1/2, y+1/2, -z+1/2, vi = -x+1/2, y-1/2, -z+1/2, vii = x-1/2, -y+3/2, z-1/2, viii = x+1/2, -y+3/2, z+1/2, ix = x+1/2, -y+3/2, z-1/2.

Table S9. Analysis of ring-interactions O-H···Cg(chelate-ring) and X···Cg(I) for **2** with standard uncertainties in parentheses.

O-H···Cg	d(H···Cg)	<(O-H···Cg)	
O(3)-H(3B)···Cg(4)	3.00(4)	72(3)	
Cl···Cg(I)	**d(Cl···Cg)**	**<(Zn-Cl···Cg)**	**Gamma**
Zn(2)-Cl(3)···Cg(2)#vi	3.4674(11)	110.76(3)	11.62
Zn(2)-Cl(3)···Cg(2)#vii	3.4674(11)	110.76(3)	11.62
Zn(2)-Cl(4)···Cg(1)	3.2821(11)	108.18(3)	3.50
Zn(2)-Cl(4)···Cg(1)#i	3.2821(11)	108.18(3)	3.50

Gamma = Angle between Cg-H vector and ring J normal. Symmetry transformations used to generate equivalent atoms: i = 1-x, 1-y, 1-z, ii = 1-x, 2-y, 1-z, iii = x-1, y, z, iv = x-1/2, -y+3/2, z+1/2, v = -x+1/2, y+1/2, -z+1/2, vi = -x+1/2, y-1/2, -z+1/2, vii = x-1/2, -y+3/2, z-1/2, viii = x+1/2, -y+3/2, z+1/2, ix = x+1/2, -y+3/2, z-1/2. Cg(1) = N1- C3-C4#i-N1#i-C3#i –C4, Cg(2) = N2- C5-C6#ii-N2#ii-C5#ii –C6, Cg(3) = Zn1-O1-C1-C3-N1, Cg(4) = Zn1-O2-C2-C5-N2.

Table S10. Short intra- and inter-molecular I···J, and halogen bond interactions for **2** with standard uncertainties in parentheses.

I···J	d(I···J)	<(X-I···J)
O(1)···O(4)#iii	2.59(3)	Zn1 118.76(9)
Halogen bond interactions		
Cl(2)···O(4)	3.29(2)	Zn(2) 88.22(7)
Cl(4)···O(4)	3.16(2)	Zn(2) 91.95
Cl(3)···O(3)#ix	3.16(2)	Zn(2) 116.66(4)
Cl(4)···O(3)#vi	3.10(2)	Zn(2) 96.42
Cl(2)···O(2)#ix	3.08(19)	Zn(2) 95.99(8)
Cl(3)···O(3)#vi	3.53(18)	Zn(2) 85.13

Symmetry transformations used to generate equivalent atoms: i = 1-x, 1-y, 1-z, ii = 1-x, 2-y, 1-z, iii = -1+x, y, z, iii = x-1, y, z, iv = x-1/2, -y+3/2, z+1/2, v = -x+1/2, y+1/2, -z+1/2, vi = -x+1/2, y-1/2, -z+1/2, vii = x-1/2, -y+3/2, z-1/2, viii = x+1/2, -y+3/2, z+1/2, ix = x+1/2, -y+3/2, z-1/2.

X-ray Crystallography of [Hg$_2$(pyzdmH$_2$)$_{0.5}$(μ-Cl)$_2$(Cl)$_2$]$_n$ (3)

Colorless block crystals of **3** grew in water and analyzed by single-crystal X-ray diffraction. The crystal has strong reflections and the diffraction pattern was almost completely indexed using APEX4 using an orientation matrix and the reciprocal lattice of the crystal showed a single phase with a point group -1 symmetry. There is maybe a very tiny small twin domain, but the contribution is indeed negligible so that the data reduction worked without any issues. The symmetry of the diffraction pattern suggested by XPREP was compatible with the anorthic space group types $P1$ and $P\bar{1}$. $P\bar{1}$ (no.2) was favored with respect to the value of |E2–1|= 0.918 which has R$_{int}$ of 3.3 % and R$_\sigma$ of 2.8 %. The hydrogen atoms attached to the two oxygen atoms from the hydroxyl groups in **pyzdmH2** (O1-H1 and O2-H2) were located in difference Fourier maps and the O1-H1 and O2-H2 bond distances geometrically restrained to 0.85 Å (DFIX 0.85 O1 H1 and DFIX 0.85 O2 H2). The largest electron density peak and hole are at a distance of 0.76 Å from Hg2

and Hg1. The electron density near Hg2 suggests the possibility of twinning. This was investigated using PLATON/TwinRotMat and APEX4, specifically by analyzing the reciprocal lattice and identifying domains. Upon analyzing the selected crystal, it was determined that there is no twin domain present. The high electron density around Hg is primarily attributed to the heavy atom, mercury (Hg). The structure refinement converged to a final value of $R1$ 2.6 % and $wR2$ 5.5 %. The X-ray diffraction experiment and structure determination details are summarized in Table S1.

Table S11. Hydrogen bond interactions for **3** [Å and °] with standard uncertainties in parentheses.

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
Intra O(1)-H(1)···O(2)#i	0.822(19)	1.93(2)	2.73(3)	165
Intra O(1)-H(1)···Cl(4)#i	0.822(19)	2.75(2)	3.12(3)	109
O(2)-H(2)···Cl(2)#iii	0.830(19)	2.82(4)	3.47(3)	136
O(2)-H(2)···O(1)#iii	0.830(19)	2.25(3)	2.96(3)	143
C(1)-H(1B)···Cl(3)#iv	0.99	2.95(9)	3.52(4)	118
Intra C(3)-H(3)···Cl(1)#i	0.95	2.81(9)	3.51(4)	131
Intra C(4)-H(4)···Cl(3)#ii	0.95	2.97(9)	3.66(4)	131
Intra C(6)-H(6B)···Cl(2)#ii	0.99	2.95(8)	3.68(4)	132
C(1)-H(1A)···Cl(1)#xiii	0.99	3.12(9)	4.08	165
C(4)-H(4)···Cl(1)#vi	0.95	3.09(8)	3.69	123
C(6)-H(6A)···Cl(1)#vi	0.99	2.99(8)	3.80	140
C(6)-H(6A)···Cl(2)#iii	0.99	3.04(9)	3.38	101
C(1)-H(1B)···Cl(2)#xiv	0.99	3.09(8)	3.40	154
C(1)-H(1B)···Cl(3)#iv	0.99	2.95(9)	3.35	118
C(3)-H(3)···Cl(3)#iv	0.95	3.02(9)	3.57	119
C(1)-H(1A)···Cl(4)#ix	0.99	2.98(9)	3.42	108

Symmetry transformations used to generate equivalent atoms: i = -x+2, -y+1, -z+1, ii = -x+1, -y+1, -z+1, iii = x, y, z-1, iv = -x+1, -y+2, -z+1, v = x, y-1, z+1, vi = 2-x, -y, 1-z, vii = x, y+1, z-1, viii = 2-x, 2-y, -z, ix = x, y, z+1, x = x, y-1, z-1, xi = 2-x, 1-y, -z, xii = x, y-1, z, xiii= x, y+1, z, xiv = 1-x, 1-y, 2-z.

Table S12. Analysis of ring-interactions Cg(I)-Cg(J) for **3**.

Cg(I)···Cg(J)	d(Cg(I)···Cg(J))	Alpha	Slippage
Cg(1)···Cg(1)#i	3.998(2)	0.03(17)	1.445
Cg(1)···Cg(1)#ii	3.941(1)	0.03(17)	1.539

Symmetry transformations used to generate equivalent atoms: i = -x+2, -y+1, -z+1, ii = 2 –x, 1–y, 1–z. Cg(1) = N1- C2-C3-N2-C5 –C4 with an r.m.s deviation of 0.004 Å. Cg-Cg distance between ring centroids (Ang.), Alpha = Dihedral angle between planes I and J (Deg) Slippage = distance between Cg(I) and perpendicular projection of Cg(J) on ring I (Ang).

Table S13. Short intra- and inter-molecular I···J, and halogen bond interactions for **3** with standard uncertainties in parentheses.

I···J	d(I···J)	<(X-I···J)
Hg(1)···Cl(4)#v	3.1820(9)	O(1) 129.27(5)
Hg(2)···Cl(2)#vii	3.4520(9)	N(2) 170.01(7)
Intra Hg(1)···Cl(3)#ii	3.1772(10)	O(1) 139.25(5)
Intra Hg(1)···Cl(4)#i	3.1623(9)	N(1) 120.34(7)
O(1)···O(2)#ix	**2.959(3)**	H(1) 89.26(9)

Halogen bond interactions

Intra Cl(4)···O(1)#vi	3.118(2)	Hg(2) 95.53(7)

Symmetry transformations used to generate equivalent atoms: i = -x+2, -y+1, -z+1, ii = -x+1, -y+1, -z+1, iii = x, y, z-1, iv = -x+1, -y+2, -z+1, v = x, y-1, z+1, vi = 2-x, -y, 1-z, vii = x, y+1, z-1, viii = 2-x, 2-y, -z, ix = x, y, z+1, x = x, y-1, z-1, xi = 2-x, 1-y, -z, xii = x, y-1, z, xiii= x, y+1, z, xiv = 1-x, 1-y, 2-z.
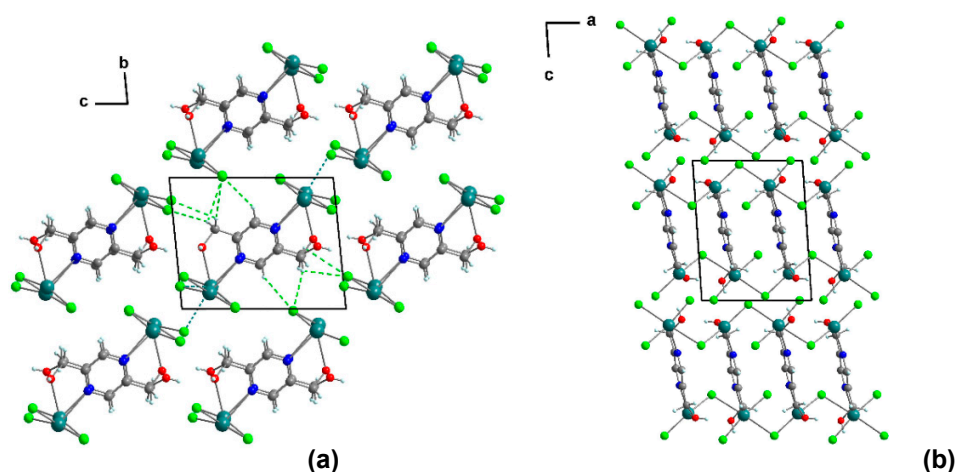
Figure S7. (a) Packing diagram of **3** along the *a*-axis, short interactions of the C-H···Cl and Cl···Hg types are depicted by dashed bonds in light green and blue-green colors **(b)** Packing diagram of **3** along the *b*-axis.

X-ray Crystallography of {[Cd$_2$(pyzdmH$_2$)(μ-Cl)$_4$]·H$_2$O}$_n$ (4)

Colorless block crystals of {[Cd$_2$(**pyzdmH$_2$**)(μ-Cl)$_4$]·H$_2$O}$_n$ grew in water and analyzed by single crystal X-ray diffraction. The crystal has strong high-resolution diffractions (0.545 Å). The diffraction pattern was almost completely indexed using APEX4 using an orientation matrix and reciprocal lattice of the crystal showed to some extent entirely single phase with a point group 2/m symmetry. The higher metric symmetry was suggested by XPREP a C-face-centered monoclinic unit cell which has R$_{sym}$ of 0.8 %. Analysis of systematic absences (suggested c/glide plane) and the value of |E2–1| = 0.887 lead to an acceptable centrosymmetric monoclinic space group *C*2/*C*. (no.15) with R$_{merge}$ and R$_σ$ of 1.86 % and 1.03 % respectively. Hydrogen atom attached to the oxygen from the hydroxyl group in **pyzdmH2** is highly disordered and can be found explicitly from Fourier difference maps. Two possible positions of the hydrogen atom were found (H1A and H1B) and refined by PART instructions and free variables number 2 (the value of 0.59 is given on the FVAR instruction) and the related distances restrained by DFIX and DANG commands (DFIX 0.85 H1A O1, DANG 1.9 0.02 C1 H1A and DFIX 0.85 H1B O1). The crytal water molecule lies on a special position (on

the twofold screw axis) and appears strongly disordered. O2, H2Aand H2B atoms with a partial occupancy value of 0.5 are refined with PART -1 and PART 0. In the refinement method, O2 was refined with an adequate thermal anisotropic displacement parameter (U_{eq} = 0.025). Finally, the O2, H2A as well as -H2B are flanked with AFIX 6 and AFIX 0. The structure refinement successfully converged to a final value of $R1$ 2.3 % and $wR2$ 6.6 %. The X-ray diffraction experiment and structure determination details are summarized in Table S1.

**Table S14.** Hydrogen bond interactions for **4** [Å and °] with standard uncertainties in parentheses.

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
O(1)-H(1A)···O(2)#x	0.85(6)	1.83(10)	2.62(10)	154
O(1)-H(1A)···O(2)#iv	0.85(6)	1.99(10)	2.69(10)	138
O(1)-H(1B)···O(1)#iv	0.85(8)	1.82(10)	2.62(5)	156
O(2)-H(2B)···O(1)#iv	0.93	1.85	2.69(10)	149
O(2)-H(2A)···Cl(2)#ii	0.80	2.65(13)	3.257(9)	134
O(2)-H(2A)···Cl(2)#v	0.80	2.68(13)	3.179(9)	122
C(1)-H(1C)···Cl(1)#iv	0.99	2.99	3.87(5)	150.0
C(1)-H(1C)···Cl(2)#vii	0.99	3.08	3.73(5)	125
Intra C(3)-H(3)···Cl(1)#ii	0.95	2.70(11)	3.434(5)	134
Intra C(1)-H(1C)···Cl(1)#viii	0.99	2.97(11)	3.87(5)	114
Intra C(3)-H(3)···Cl(2)	0.95	2.91(14)	3.57(5)	128
Intra O(1)-H(1A)···Cl(1)#i	0.85(6)	2.85(10)	3.28(5)	114

Symmetry transformations used to generate equivalent atoms: i = -x+1, y, -z+1/2, ii = -x+1,-y+1,-z+1, iii = -x+1/2,-y+1/2,-z+1, iv = -x+1,-y,-z+1, v = x, 1-y, 1/2+z, vi = x, -y, 1/2+z, vii = x, -1+y, z, viii = x-1/2, y-1/2, z, ix = x, y+1, z, x = x, -y, z-1/2.

Table S15. Short intra- and inter-molecular I···J, and halogen bond interactions for **4** with standard uncertainties in parentheses.

I···J	d(I···J)	<(X-I···J)
O(2)···Cl(2)#ii	3.257(8)	Cd 133.35(16)
O(2)···Cl(2)#v	3.179(8)	Cd 137.70(16)
O(2)···Cl(1)#iv	3.402(8)	Cd 86.80(16)
Intra O(1)···Cl(1)#i	3.281(4)	H(1B) 143(8)

Symmetry transformations used to generate equivalent atoms: i = -x+1,y,-z+1/2, ii = -x+1,-y+1,-z+1, iii = -x+1/2,-y+1/2,-z+1, iv = -x+1,-y,-z+1, v = x, 1-y, 1/2+z, vi = x, -y, 1/2+z, vii = x, -1+y, z, viii = x-1/2, y 1/2, z, ix = x, y+1, z,

X-ray Crystallography of {[Cd$_2$(pyzdmH2)(μ-Br)$_4$] .H$_2$O}$_n$ (5)

Yellowish colored block crystals of {[Cd$_2$(**pyzdmH2**)(μ-Br)$_4$] .H$_2$O}$_n$ grew in water and analyzed by single crystal X-ray diffraction. The crystal does not have strong reflections specially at the high resolutions. The diffraction pattern was almost completely indexed using APEX4 using an orientation matrix and reciprocal lattice of the crystal showed an almost entirely single phase with a point group 2/m symmetry. The higher metric symmetry was suggested by XPREP a face-center monoclinic unit cell which has R$_{sym}$ of 3.3 %. Analysis of systematic absences (suggested c/glide plane) and the value of |E2–1|= 0.934 lead to an acceptable centrosymmetric monoclinic space group $P2$/c. (no.15) with R$_{merge}$ and R$_\sigma$ of 3.02 % and 6.15 % respectively. Two possible positions of the hydrogen atom were found (H1A and H1B) and refined by PART instructions and free variables number 2 (the value of 0.72 is given on the FVAR instruction) and the related distances restrained by DFIX and DANG commands (DFIX 0.85 H1A O1, DANG 1.9 0.02 C1 H1A and DFIX 0.85 H1B O1). The crystal water molecule which lies near a special position (the twofold screw axis) was largely disordered. In the refinement method, O2, H2Aand H2B atoms with a partial occupancy value of

0.5 are refined with PART -1 and PART 0 and O2, H2A as well as -H2B are flanked with AFIX 6 and AFIX 0. Finally, in the refinement method, the electron density around O2 dropped and O2 was refined with an adequate thermal anisotropic displacement parameter (U_{eq} = 0.032). The structure refinement successfully converged to a final value of $R1$ 4.4 % and $wR2$ 7.4 %. The X-ray diffraction experiment and structure determination details are summarized in Table S1.

Table S16. Hydrogen bond interactions for **5** [Å and °] with standard uncertainties in parentheses.

| D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
O(1)-H(1A)#vi···O(2)	0.85(6)	1.83(7)	2.68(10)	172(8)
O(1)-H(1B)#v···O(1)#ii	0.85(6)	1.81(9)	2.64(5)	165(12)
O(2)-H(2B)···O(1)#v	0.72	1.99	2.70(10)	165
O(2)-H(2A)···Br(2)	0.84	2.78	3.39(9)	131
O(2)-H(2A)···Br(2)#i	0.84	2.88	3.33(9)	115
O(2)-H(2B)···Br(1)#v	0.72	3.19	3.43(10)	103
C(1)-H(1C)···Br(1)#ix	0.99	3.10	3.997(5)	152
C(1)-H(1C)···Br(2)#iv	0.99	3.23	3.88(5)	125
Intra C(3)-H(3)···Br(1)#ii	0.95	2.87	3.615(5)	136
Intra H(1C)···Br(1)#x	0.99	3.04	3.582(5)	115
Intra C(3)-H(3)···Br(2)	0.95	2.97	3.66(5)	130.0
Intra O(1)-H(1A)#vi ···Br(1)#v	0.85(6)	3.13(7)	3.40(5)	65

Symmetry transformations used to generate equivalent atoms: i = -x+1, y, -z+3/2, ii = -x+1, -y+1, -z+1, iii = -x+3/2, -y+1/2,-z+1, iv = x, y-1, z, v = x, y+1, z, vi = 1-x, y+1, 3/2-z, vii = 1-x, y-1, 3/2-z, viii = -x+1,3-y,1-z, ix = -x+1,-y,1-z, x = x+1/2, 1/2+y, z.

Table S17. Short intra- and inter-molecular I···J, and halogen bond interactions for **5** with standard uncertainties in parentheses.

I···J	d(I···J)	<(X-I···J)
O(2)···Br(2)	3.394(9)	Cd 135.92(16)
O(2)···Br(2)#i	3.328(9)	Cd 140.41(17)
O(2)···Br(1)#v	3.428(9)	Cd 84.75(8)

Symmetry transformations used to generate equivalent atoms: ix = -x+1, -y, 1-z.

(a)

(b)
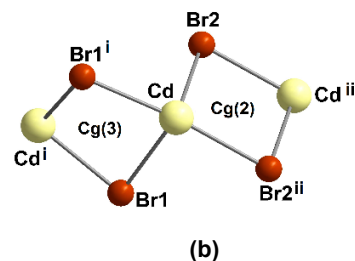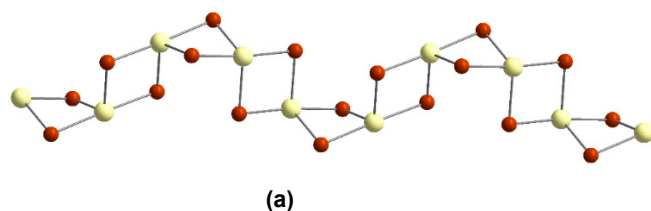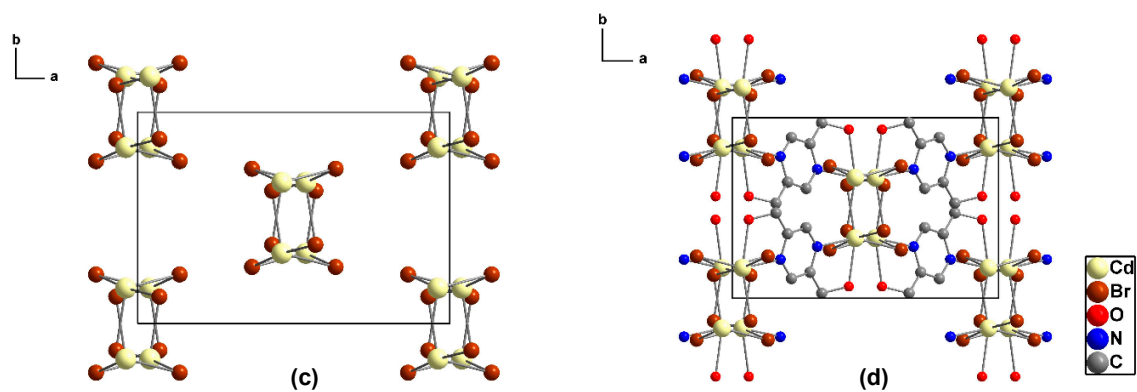
Figure S8. **(a**) One-dimensional crenellation-like chain in **5**. **(b)** Two alternating square-like rings, (Cg(2) = Cd-Br2-Cd^{ii}-Br2^{ii} r.m.s deviation of 0.000 Å and Cg(3) = Cd-Br1-Cd^{i}-Br^{i} r.m.s deviation of 0.291 Å. **(b)** The dihedral angle between adjacent 4-membered rings in the chain is 82.91°. **(c)** Ball and stick presentation of five crenellation-like chains. **(d)** The unit cell of 3D network **5** viewed along the *c*-axis. For the sake of clarify, hydrogen atoms and crystal water molecules omitted. Symmetry codes: i = -x+1, y, -z+3/2, ii = -x+1, -y+1.
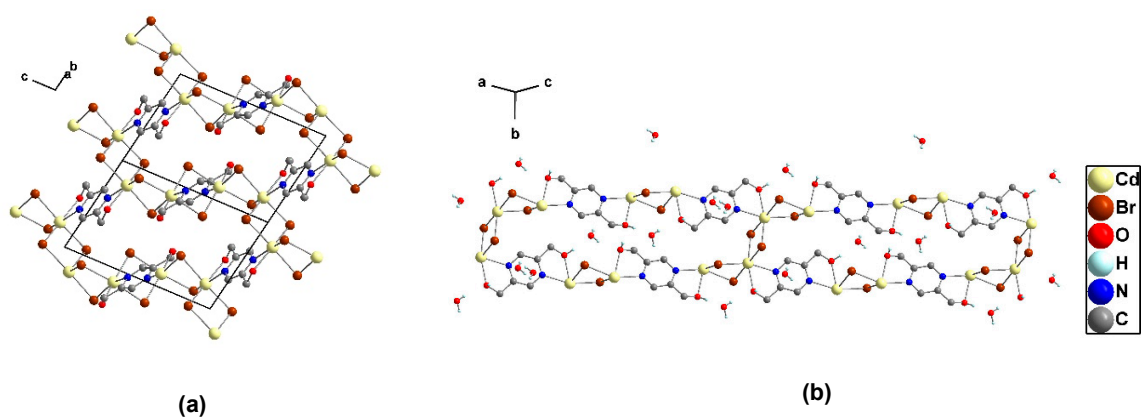
Figure S9. (a) The unit cell packing within the *bc* plane in **5**. For the sake of clarify, water molecules were omitted. **(b)** The simplified view of the empty spaces with crystal water molecules in **5**.

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Section S3. Infrared spectra of compounds **2, 3** and **5.**
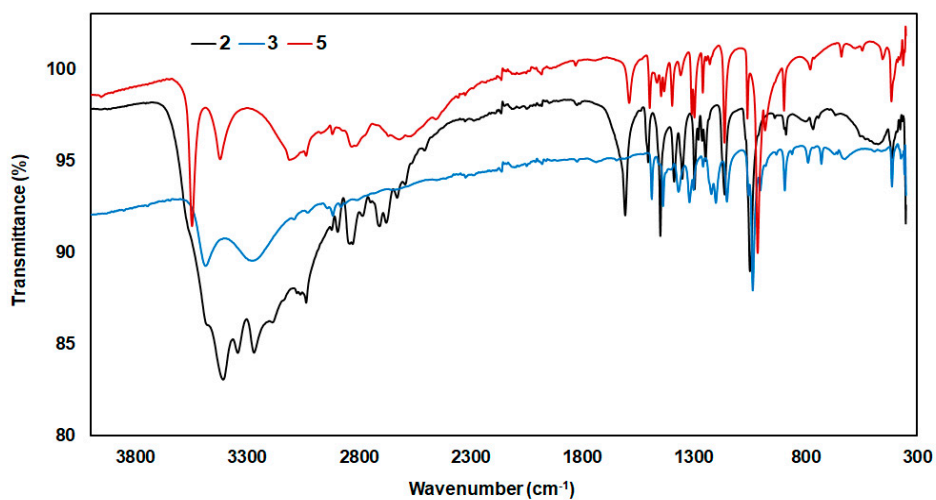
Figure S10. IR spectra of **2, 3** and **5**.
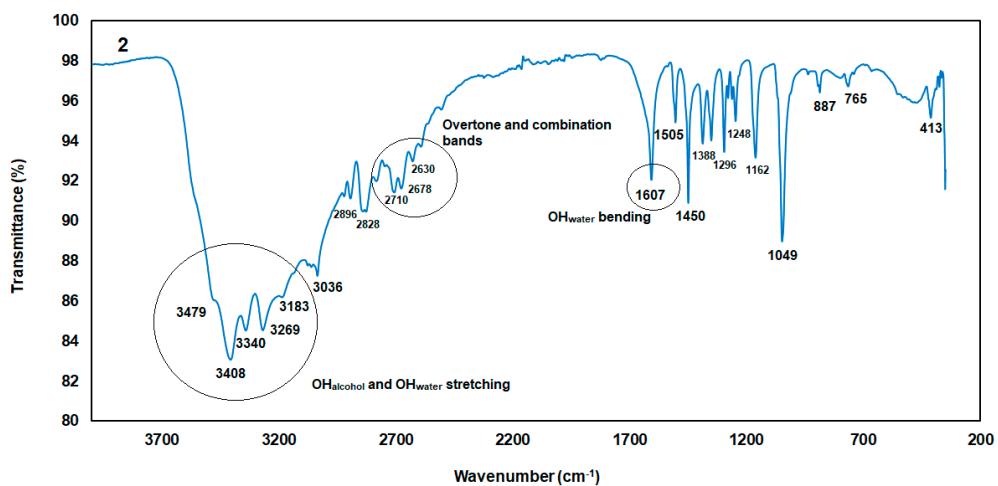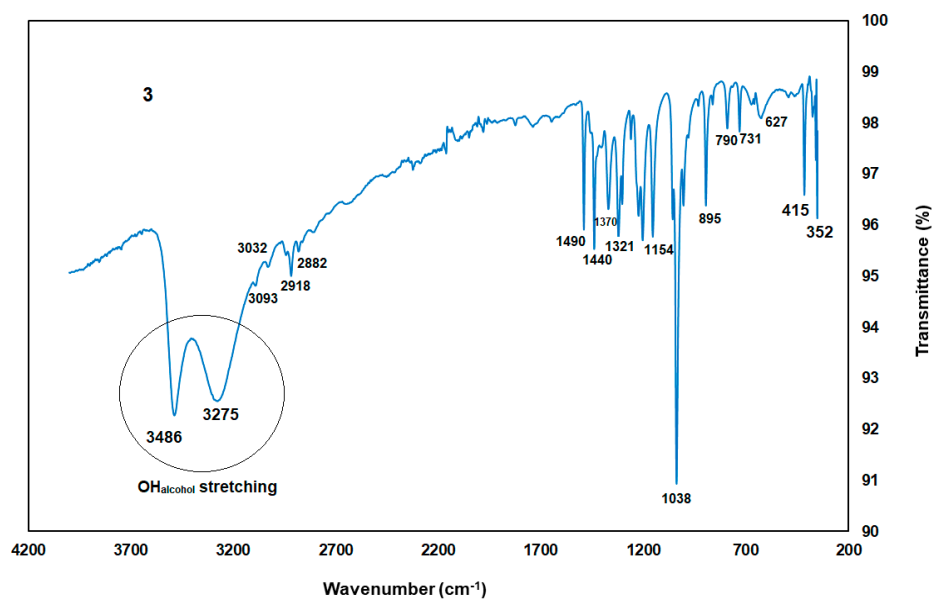

Figure S11. IR spectrum of **2**.
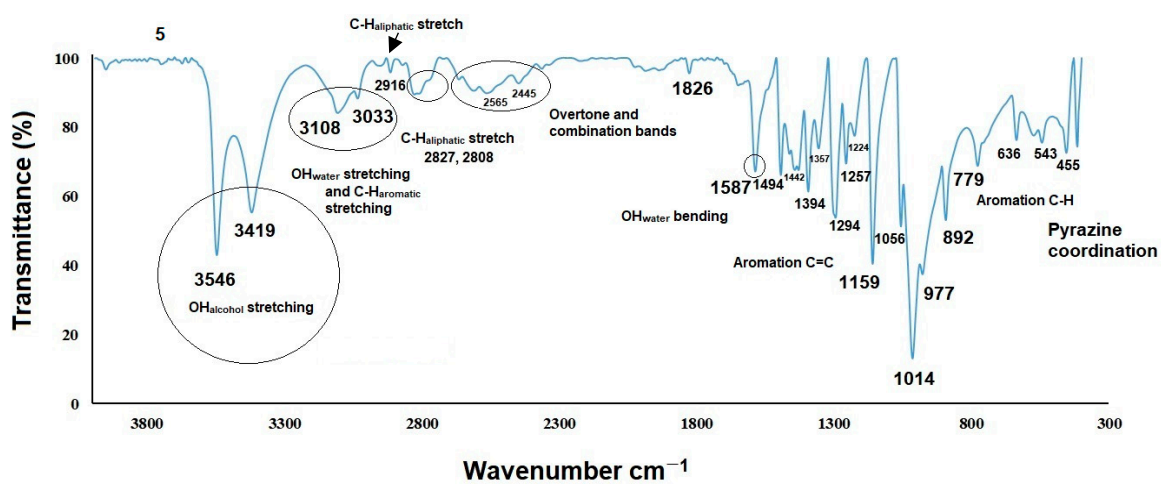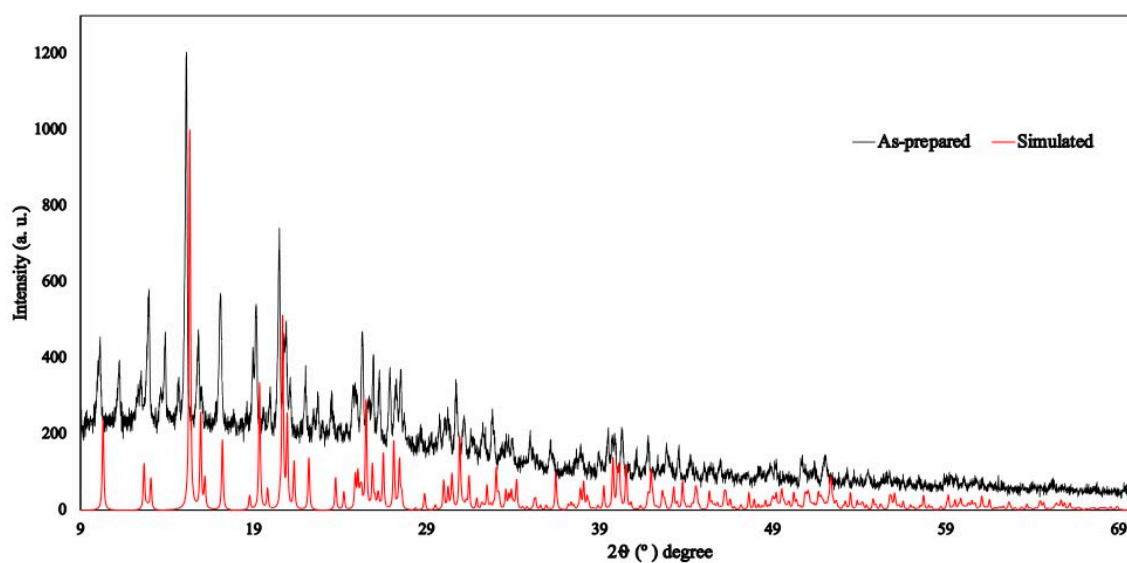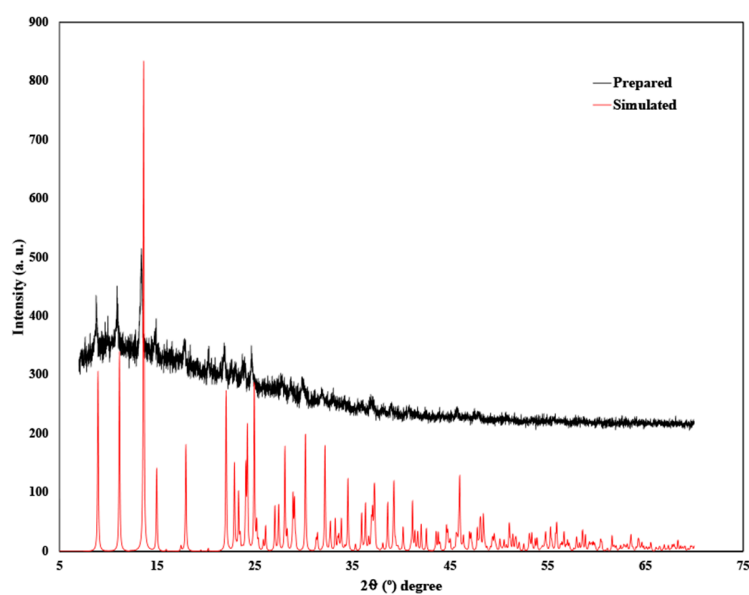
Figure S12. IR spectrum of **3**.

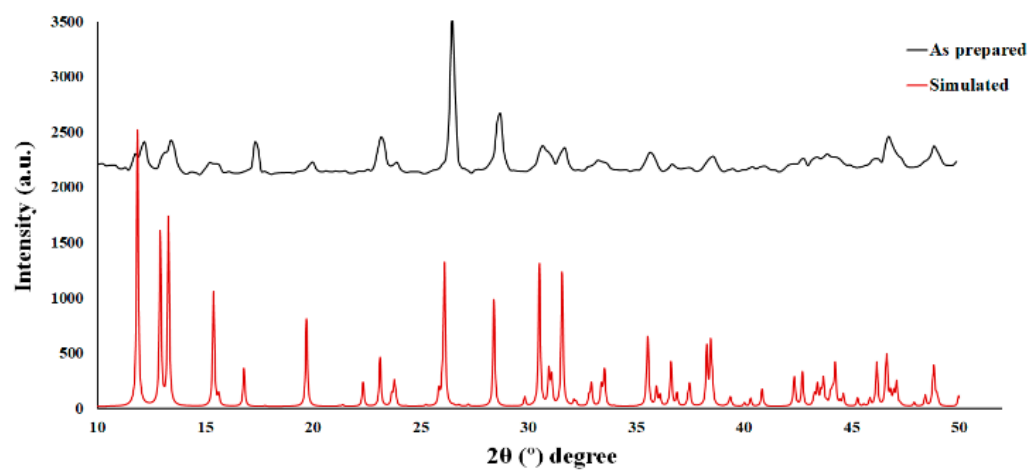
Figure S13. IR spectrum of **5**.

Section S4. Powder X-ray diffractograms of compounds **2**, **3** and **5**.

Figure S14. Experimental (black) and simulated (red) powder X-ray diffractogram of **2**.

Figure S15. Experimental (black) and simulated (red) powder X-ray diffractogram of **3**.

Figure S16. Experimental (black) and simulated (red) powder X-ray diffractogram of **5**.