Electronic Supplementary Material (ESI) for CrystEngComm
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LUMINESCENCE AND MAGNETIC PROPERTIES OF THREE METAL-ORGANIC FRAMEWORKS BASED ON 5-(1*H*-TETRAZOL-5-YL)ISOPHTHALIC ACID LIGAND

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Index

1. Synthesis

{[$Cd_4(TZI)_2(OH)_2(H_2O)_4](H_2O)_6$}$_n$ (1): A mixture of $CdCl_2$(366 mg, 2 mmol), 5-(1H-cyano-5-yl)isophthalic acid (191 mg, 1 mmol), sodium azide (65 mg, 1 mmol) and water (14 mL) was sealed in a Teflon-lined acid digestion autoclave and heated at 140°C under autogenous pressure. After 12 h of heating, the reaction vessel was cooled down to room temperature during a period of 2 h. Colourless crystals of 1 were obtained and were washed with H_2O. Yield: 70% based on Cd. Anal. Calcd for (Cd4C18N8O20H28): C 19.05, H 2.49, N 9.90. Experimental : C 19.37, H 2.59, N 9.76. FT-IR (KBr pellet): 3410 (m), 3131 (s), 1618 (m), 1563 (m), 1398 (s), 1384 (s), 757 (w) cm^{-1}

{[$Zn_2(TZI)(OH)(H_2O)_2$] (H_2O)}$_n$ (2): Compound 2 was prepared similar to that of compound 1, but the $ZnCl_2$ (272 mg, 2 mmol) was used instead of $CdCl_2$.Colourless crystals of 2 were obtained and were washed with H_2O. Yield: 45% based on Cd. Anal. Calcd for (Zn2C9N4O8H10): C 25.12, H 2.34, N 13.03. Experimental : C 25.37, H 2.51, N 12.87. FT-IR (KBr pellet): 3388 (s), 1622 (m), 1575 (s), 1450 (m), 1392 (s), 1244 (m), 1105 (w), 759 (m), 729 (m) cm^{-1}

{[$Co_8(TZI)_3(OH)_5((N_3)_2(H_2O)_8](H_2O)_8$}$_n$ (3): Compound 3 was prepared similar to that of compound 1, but the $CoCl_2 \cdot 6H_2O$ (476 mg, 2 mmol) was used instead of $CdCl_2$. Pink crystals of 3 were obtained and were washed with H_2O. Yield: 30% based on Cd. Anal. Calcd for (Co8C27N18O33H46): C 19.98, H 2.86, N 15.54. Experimental : C 20.17, H 3.01, N 15.37. FT-IR (KBr pellet): 3427 (s), 2085 (m), 1623 (m), 1576 (m), 1457 (m), 1373 (s), 763 (w), 724 (m) cm^{-1}

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2. Crystal Structures Pictures

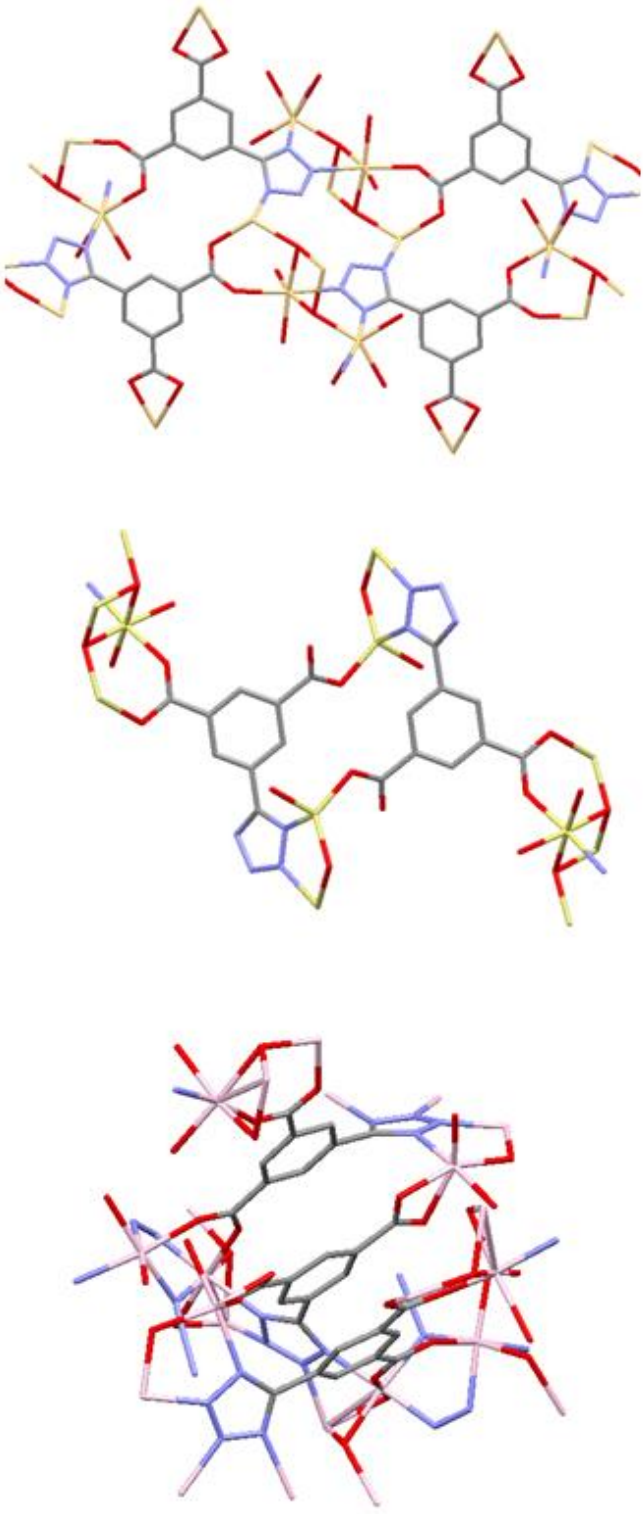

Figure S1. A view of the metal environment and coordination mode of the ligand for **1** (up), **2**(middle) and **3** (down).

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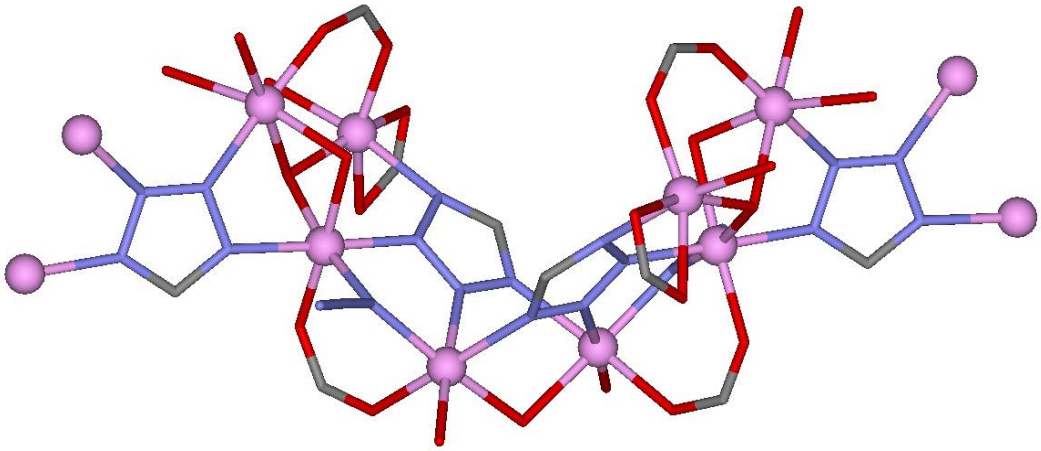

Figure S2. Helical Co(II) chains in **3** generated by hydroxyl, carboxylate, azide and tetrazolate-bridged groups.

3. Luminescence Properties

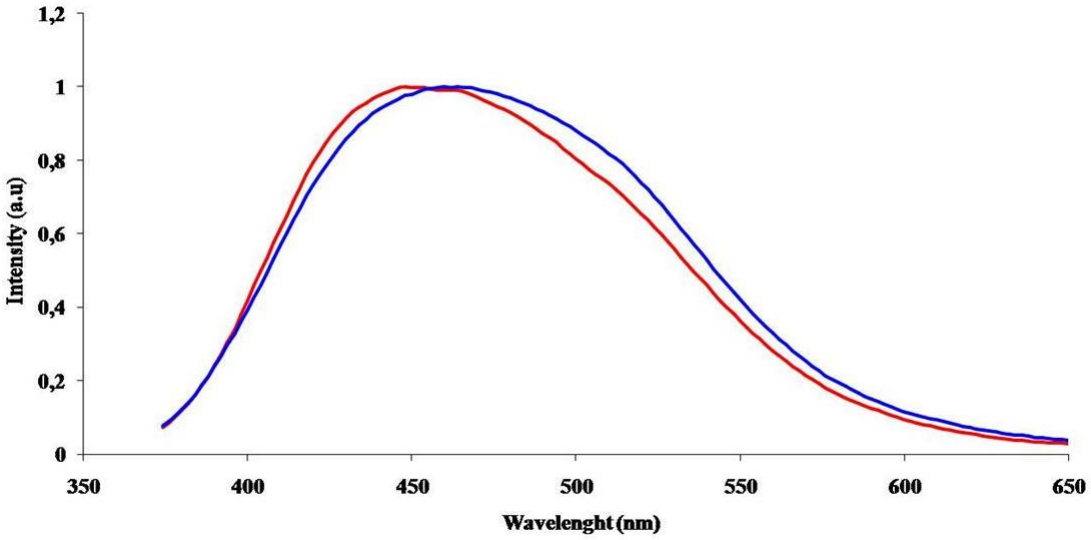

Figure S3. Emission spectra of **1** (blue line) and **2** (red line) at room temperature in solid state. Horizontal axis: wavelength (nm); vertical axis: intensity (a.u.).

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4. Field dependence of the Magnetization.

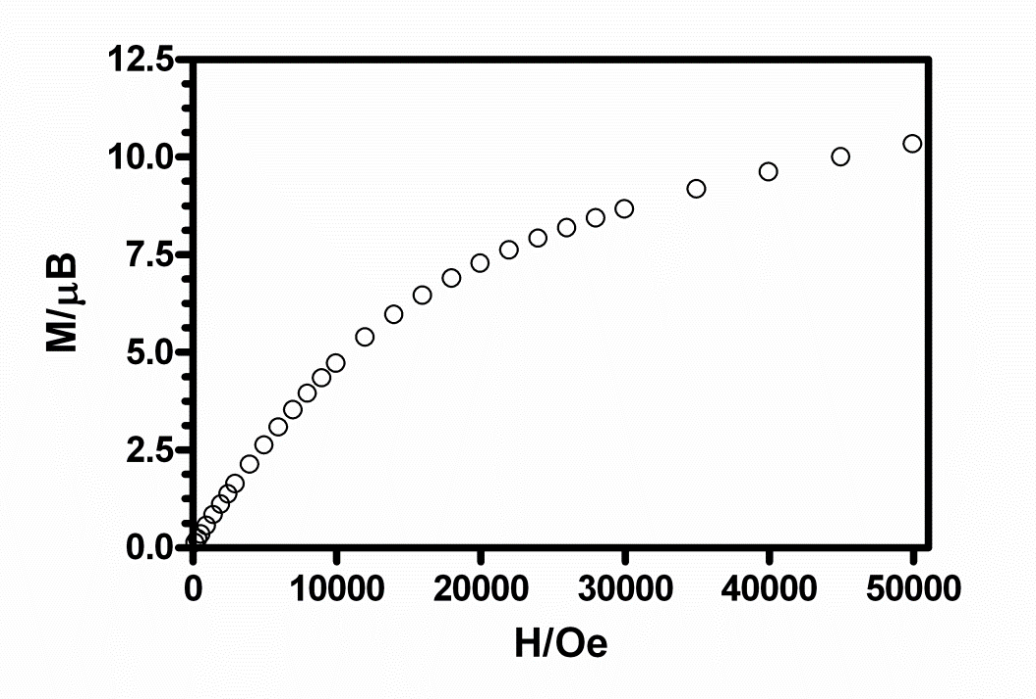

Figure S4.- Field dependence of the Magnetization for **3**.

5. Single-Crystal Structure Determination.

Suitable crystals of **1** were mounted on glass fiber and used for data collection. Data were collected with a Bruker AXS APEX CCD area detector equipped with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) by applying the ω-scan method and a StadiVari Stoe. The data were processed with APEX2[1] and corrected for absorption using SADABS.[2] The structure was solved by direct methods using SIR97,[3] revealing positions of all non-hydrogen atoms. These atoms were refined on F^2 by a full matrix least-squares procedure using anisotropic displacement parameters.[4] Aromatic hydrogen atoms were included as fixed contributions riding on attached atoms with isotropic thermal displacement parameters 1.2 times those of the respective atom. The structure has disorder problems with solvent molecules. Attempts to identify the solvent molecules failed in compound **2** and **3**. Instead, a new set of F^2 (*hkl*) values with the contribution from solvent molecules withdrawn was obtained by the SQUEEZE procedure implemented in PLATON-94.[5] Refinement reduced R_1 to 0.042 and 0.083 for **2** and **3**, respectively. Final R(F), wR(F^2) and goodness of fit agreement factors, details on the data collection and analysis can be found in Table S1. Crystallographic data (excluding structure factors) for the reported structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 928815 and 928816 for **2** and **3**, respectively. Copies of the data can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44)1223 336-033; e-mail, deposit@ ccdc.cam.ac.uk).

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6. Crystal Data

Table S1. Crystallographic Data and Structural Refinement Details for **1-3**

compound	**1**	**2**	**3**
chemical formula	$C_{18}H_{28}N_8O_{20}Cd_4$	$C_9H_{10}N_4O_8Zn_2$	$C_{27}H_{46}N_{18}O_{33}Co_8$
CCDC	ESI	928815	928816
M/gmol^{-1}	1126.08	432.95	1622.26
T (K)	293	293	293
λ/Å	0.71073	0.71073	0.71073
cryst syst	triclinic	triclinic	orthorhombic
space group	*P-1*	*P-1*	*Pbcn*
a/ Å	6.8383(12)	7.711(3)	13.739(2)
b/ Å	10.3778(15)	8.959(3)	24.301(3)
c/ Å	24.2312(14)	9.103(3)	15.179(2)
α/deg	100.651(9)	88.460(5)	90
β/deg	90.439(8)	88.793(4)	90
γ/deg	108.757(6)	74.567(5)	90
V/ Å^3	1596.1(4)	605.9(4)	5067.8(12)
Z	2	2	4
ρ(g cm-3)	2.343	2.373	2.126
μ(mm-1)	2.726	4.016	2.671
Unique reflections	8273	3542	89774
R(*int*)	0.0357	0.020	0.1356
GOF on F^2	1.299	1.033	0.581
R1 [$I > 2\sigma(I)$]	0.159	0.042	0.083
wR2 [$I > 2\sigma(I)$]	0.388	0.101	0.206

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$, $wR(F^2) = [\sum w(F_o^2 - F_c^2)^2/\sum wF^4]^{1/2}$

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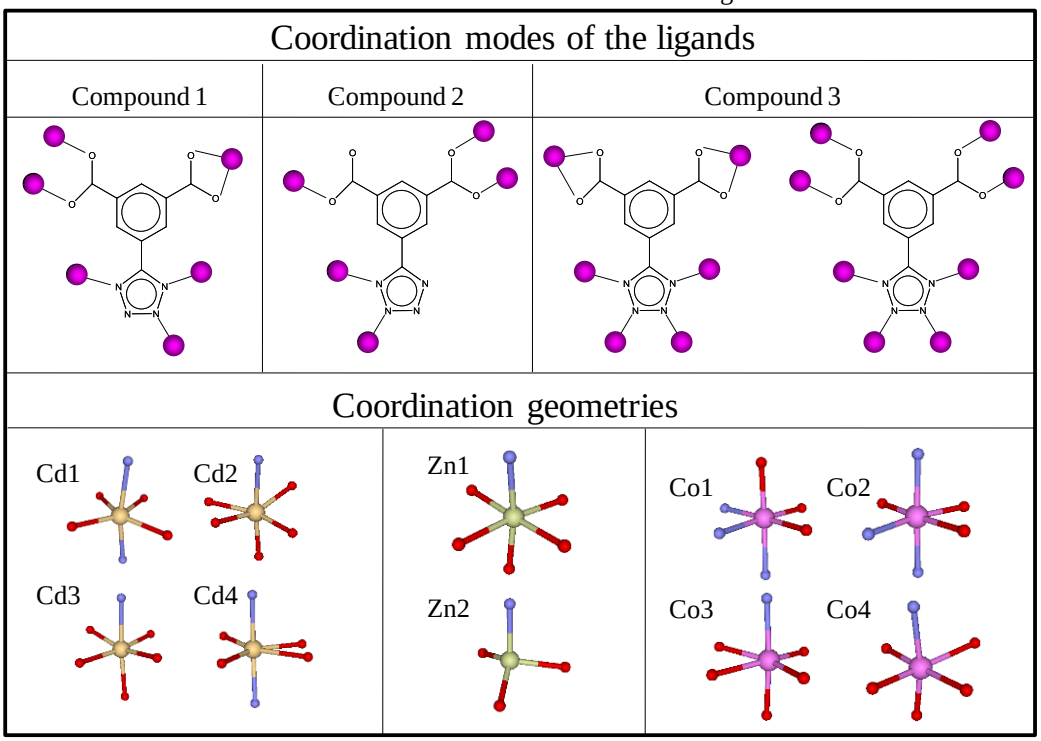
Table S2. Selected Distances (Å) for compound **1**, **2** and **3**

1	**2**	**3**
Cd1 O1C 2.19(3)	Zn1 O1 2.067(3)	Co1 O2W 2.025(6)
Cd1 O4B 2.23(3)	Zn1 O1A 2.085(3)	Co1 O1 2.066(5)
Cd1 O2B 2.34(3)	Zn1 O1A 2.116(3)	Co1 N3 2.094(7)
Cd1 N4A 2.41(3)	Zn1 N2 2.128(4)	Co1 N7 2.110(7)
Cd1 O1B 2.44(3)	Zn1 O1W 2.132(3)	Co1 O2A 2.153(6)
Cd1 N1A 2.45(3)	Zn1 O2W 2.134(3)	Co1 N4 2.201(7)
Cd1 C8B 2.71(4)	Zn1 Zn1 3.1322(12)	Co2 O2 2.012(6)
Cd2 O3B 2.23(3)	Zn2 O4 1.941(3)	Co2 N2 2.040(6)
Cd2 O1C 2.28(3)	Zn2 O1A 1.955(3)	Co2 N7 2.057(7)
Cd2 O1C 2.29(3)	Zn2 O2 2.017(3)	Co2 O1A 2.058(7)
Cd2 O2W 2.30(5)	Zn2 N1 2.018(4)	Co2 N5 2.092(7)
Cd2 O1W 2.32(2)		Co2 O3A 2.168(7)
Cd2 N3A 2.50(3)		Co3 O4 1.992(6)
Cd2 Cd2 3.359(7)		Co3 O1A 2.093(7)
Cd3 O2C 2.22(3)		Co3 O6 2.160(6)
Cd3 O2C 2.24(3)		Co3 N1 2.174(8)
Cd3 O4W 2.29(4)		Co3 O5 2.176(6)
Cd3 O3W 2.31(3)		Co3 O1W 2.182(8)
Cd3 N2B 2.32(3)		Co3 C15 2.501(9)
Cd3 O1A 2.35(3)		Co4 O3 1.937(8)
Cd3 Cd3 3.354(5)		Co4 O3A 2.087(8)
Cd4 O2C 2.25(3)		Co4 O3W 2.150(18)
Cd4 O2A 2.25(3)		Co4 N6 2.182(8)
Cd4 N4B 2.32(4)		Co4 O1A 2.264(8)
Cd4 N1B 2.34(3)		Co4 O4W 2.34(2)
Cd4 O4A 2.35(3)		

Table S3. Selected Bond Angles (Å) for compound **1**, **2** and **3**

1		**2**	**3**	
O1C Cd1 O4B 111.7(10)	O2W Cd2 Cd2 135.4(12)	O1 Zn1 O1A 90.50(12)	O2W Co1 O1 92.9(2)	O4 Co3 N1 97.0(3)
O1C Cd1 O2B 149.4(9)	O1W Cd2 Cd2 118.3(6)	O1 Zn1 O1A 91.63(12)	O2W Co1 N3 176.6(3)	O1A Co3 N1 91.3(3)
O4B Cd1 O2B 98.8(10)	N3A Cd2 Cd2 79.3(7)	O1A Zn1 O1A 83.57(12)	O1 Co1 N3 89.7(3)	O6 Co3 N1 95.6(3)
O1C Cd1 N4A 89.3(11)	O2C Cd3 O2C 82.6(11)	O1 Zn1 N2 171.92(13)	O2W Co1 N7 95.3(3)	O4 Co3 O5 152.5(3)
O4B Cd1 N4A 90.8(11)	O2C Cd3 O4W 162.5(12)	O1A Zn1 N2 97.25(13)	O1 Co1 N7 89.4(3)	O1A Co3 O5 102.0(3)
O2B Cd1 N4A 93.7(10)	O2C Cd3 O4W 99.9(13)	O1A Zn1 N2 91.49(13)	N3 Co1 N7 86.9(3)	O6 Co3 O5 59.9(2)
O1C Cd1 O1B 95.0(9)	O2C Cd3 O3W 89.5(11)	O1 Zn1 O1W 84.63(14)	O2W Co1 O2A 92.6(2)	N1 Co3 O5 80.8(3)
O4B Cd1 O1B 153.3(10)	O2C Cd3 O3W 172.0(11)	O1A Zn1 O1W 173.92(14)	O1 Co1 O2A 88.8(2)	O4 Co3 O1W 91.5(4)
O2B Cd1 O1B 54.6(9)	O4W Cd3 O3W 87.1(13)	O1A Zn1 O1W 92.92(13)	N3 Co1 O2A 85.2(3)	O1A Co3 O1W 85.8(3)
N4A Cd1 O1B 90.1(11)	O2C Cd3 N2B 79.0(10)	N2 Zn1 O1W 87.77(14)	N7 Co1 O2A 171.9(2)	O6 Co3 O1W 84.6(3)
O1C Cd1 N1A 85.0(9)	O2C Cd3 N2B 85.8(11)	O1 Zn1 O2W 89.84(13)	O2W Co1 N4 92.9(2)	N1 Co3 O1W 171.4(4)
O4B Cd1 N1A 100.1(10)	O4W Cd3 N2B 83.9(13)	O1A Zn1 O2W 95.03(12)	O1 Co1 N4 172.9(2)	O5 Co3 O1W 92.0(3)
O2B Cd1 N1A 86.5(9)	O3W Cd3 N2B 91.1(11)	O1A Zn1 O2W 177.97(11)	N3 Co1 N4 84.4(3)	O4 Co3 C15 121.8(3)
N4A Cd1 N1A 168.9(11)	O2C Cd3 O1A 103.6(11)	N2 Zn1 O2W 87.23(14)	N7 Co1 N4 94.1(3)	O1A Co3 C15 132.7(3)
O1B Cd1 N1A 81.0(9)	O2C Cd3 O1A 91.3(11)	O1W Zn1 O2W 88.61(14)	O2A Co1 N4 86.8(2)	O6 Co3 C15 29.0(2)
O1C Cd1 C8B 122.6(10)	O4W Cd3 O1A 93.7(13)	O1 Zn1 Zn1 91.44(9)	O2 Co2 N2 89.9(3)	N1 Co3 C15 86.4(3)
O4B Cd1 C8B 125.5(11)	O3W Cd3 O1A 92.1(12)	O1A Zn1 Zn1 42.16(8)	O2 Co2 N7 95.2(3)	O5 Co3 C15 31.0(2)
O2B Cd1 C8B 26.8(10)	N2B Cd3 O1A 175.9(12)	O1A Zn1 Zn1 41.40(8)	N2 Co2 N7 88.2(3)	O1W Co3 C15 89.7(3)
N4A Cd1 C8B 94.1(11)	O2C Cd3 Cd3 41.5(8)	N2 Zn1 Zn1 95.83(10)	O2 Co2 O1A 93.6(3)	O3 Co4 O3A 90.4(4)
O1B Cd1 C8B 27.9(10)	O2C Cd3 Cd3 41.1(7)	O1W Zn1 Zn1 134.12(10)	N2 Co2 O1A 88.3(3)	O3 Co4 O3W 82.5(5)
N1A Cd1 C8B 81.2(10)	O4W Cd3 Cd3 138.3(11)	O2W Zn1 Zn1 137.17(9)	N7 Co2 O1A 170.6(3)	O3A Co4 O3W 100.1(5)
O3B Cd2 O1C 90.4(10)	O3W Cd3 Cd3 131.0(8)	O4 Zn2 O1A 122.41(13)	O2 Co2 N5 90.1(3)	O3 Co4 N6 170.2(4)
O3B Cd2 O1C 104.6(10)	N2B Cd3 Cd3 79.9(8)	O4 Zn2 O2 99.30(12)	N2 Co2 N5 177.3(3)	O3A Co4 N6 83.4(3)
O1C Cd2 O1C 85.5(9)	O1A Cd3 Cd3 99.9(8)	O1A Zn2 O2 115.31(12)	N7 Co2 N5 94.5(3)	O3W Co4 N6 91.1(5)
O3B Cd2 O2W 95.4(14)	O2C Cd4 O2A 111.1(10)	O4 Zn2 N1 121.15(14)	O1A Co2 N5 89.0(3)	O3 Co4 O1A 98.7(3)
O1C Cd2 O2W 96.1(13)	O2C Cd4 N4B 84.5(12)	O1A Zn2 N1 97.83(14)	O2 Co2 O3A 177.5(3)	O3A Co4 O1A 81.6(3)
O1C Cd2 O2W 159.9(13)	O2A Cd4 N4B 98.8(12)	O2 Zn2 N1 99.40(13)	N2 Co2 O3A 91.8(3)	O3W Co4 O1A 178.0(6)
O3B Cd2 O1W 88.7(9)	O2C Cd4 N1B 86.4(11)		N7 Co2 O3A 86.8(3)	N6 Co4 O1A 87.9(3)
O1C Cd2 O1W 160.5(8)	O2A Cd4 N1B 91.0(11)		O1A Co2 O3A 84.6(3)	O3 Co4 O4W 99.1(6)
O1C Cd2 O1W 75.9(8)	N4B Cd4 N1B 168.5(13)		N5 Co2 O3A 88.1(3)	O3A Co4 O4W 166.4(6)
O2W Cd2 O1W 103.4(13)	O2C Cd4 O4A 148.4(11)		O4 Co3 O1A 105.4(3)	O3W Co4 O4W 90.8(7)
O3B Cd2 N3A 173.7(11)	O2A Cd4 O4A 100.5(11)		O4 Co3 O6 93.3(3)	N6 Co4 O4W 88.4(6)
O1C Cd2 N3A 85.0(10)	N4B Cd4 O4A 90.0(13)		O1A Co3 O6 159.2(3)	O1A Co4 O4W 87.4(6)
O1C Cd2 N3A 79.3(9)	N1B Cd4 O4A 94.2(11)			
O2W Cd2 N3A 80.9(13)	O2C Cd4 O3A 94.5(10)			
O1W Cd2 N3A 97.0(9)	O2A Cd4 O3A 154.3(10)			
O3B Cd2 Cd2 100.2(8)	N4B Cd4 O3A 85.5(12)			
O1C Cd2 Cd2 42.9(6)	N1B Cd4 O3A 88.4(10)			
O1C Cd2 Cd2 42.7(6)	O4A Cd4 O3A 54.0(10)			

Table S4. Coordination modes and coordination geometries



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7. Le Bail Refinements.

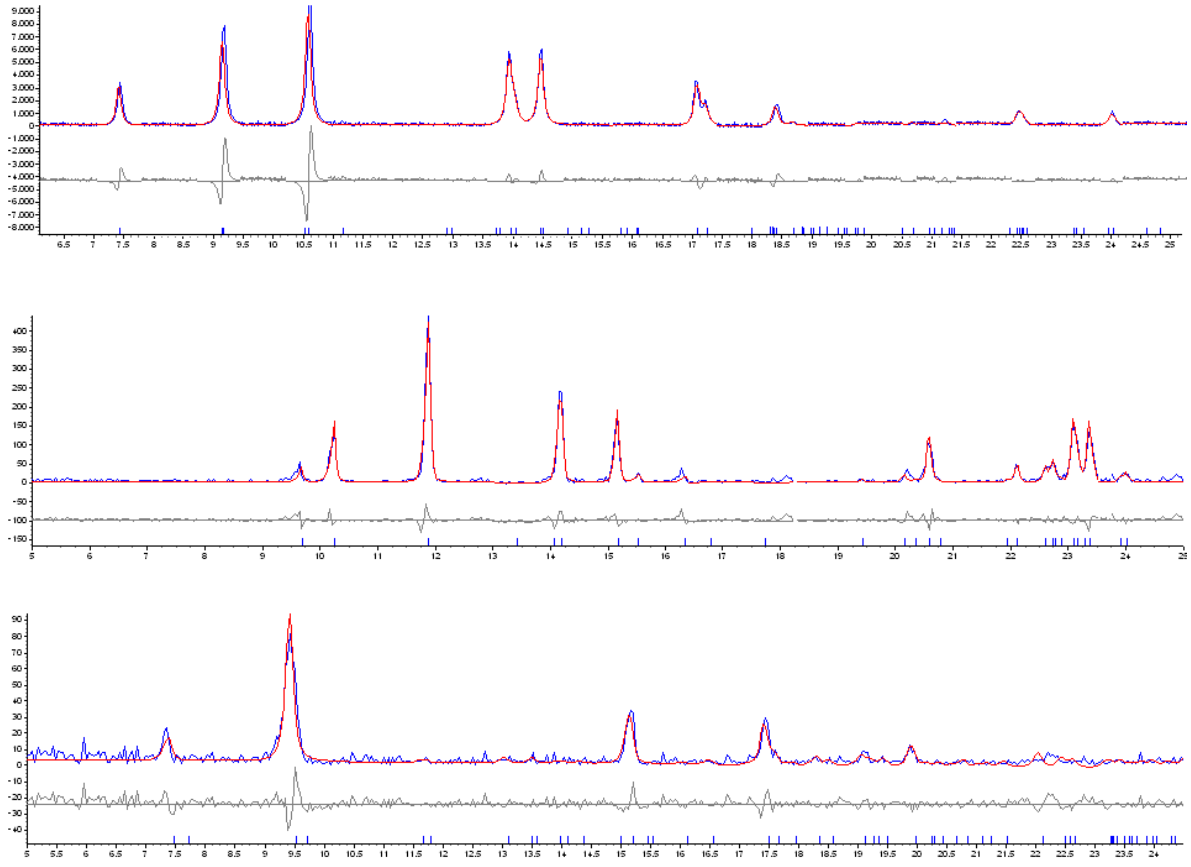

Figure S5. Le Bail Refinements for **1** (up), **2** (middle) and **3** (down) to clarify the purity of the samples.

1.- Bruker Apex2, Bruker AXS Inc, Madison, Wisconsin, USA, 2004.
2.- G. M. Sheldrick, SADABS, Program for Empirical Adsorption Correction, Institute for Inorganic Chemistry, University of Göttingen, Germany, 1996.
3.- A. Altomare, M. C. Burla, M. Camilla, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori and R. Spagna, J. Appl. Crystallogr., 1999, 32, 115.
4.-G. M. Sheldrick, SHELX97, Program for Crystal Structure Refinement, University of Göttingen, Göttingen, Germany, 1997.
5 .- A. L. Spek, PLATON-94 (V-101094),AMultipurposeCrystallographic Tool, University of Utrecht, The Netherlands, 1994.