Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information for

Discrete and polymeric cobalt organophosphates: Isolation of a 3-D cobalt phosphate framework exhibiting selective CO_2 capture

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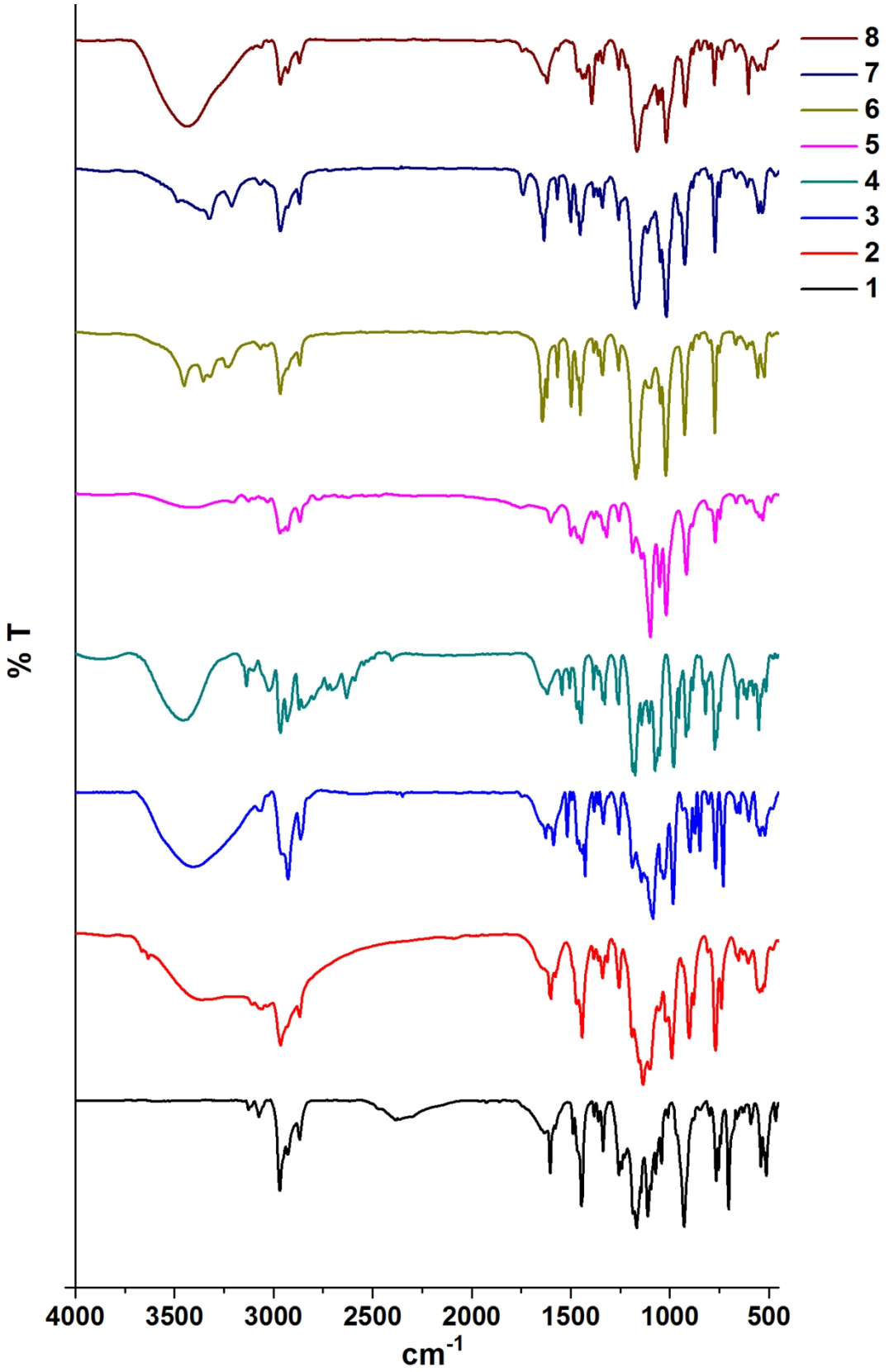

Figure S1. FT-IR spectra of compound **1**-**8**.

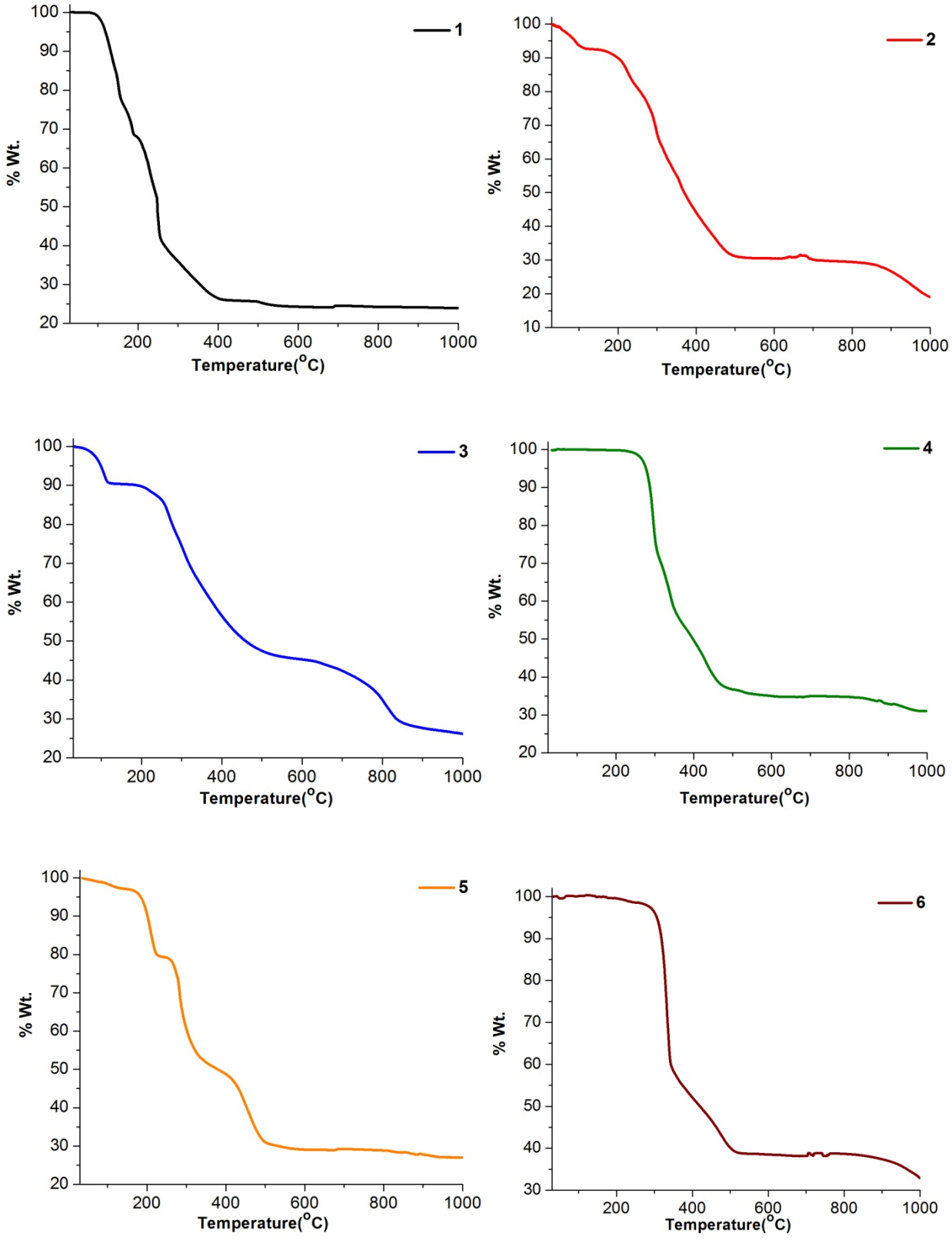

Figure S2. TGA profile of compound **1-8**.

Figure S2. Thermogravimetric Analysis of compound **1-6**.

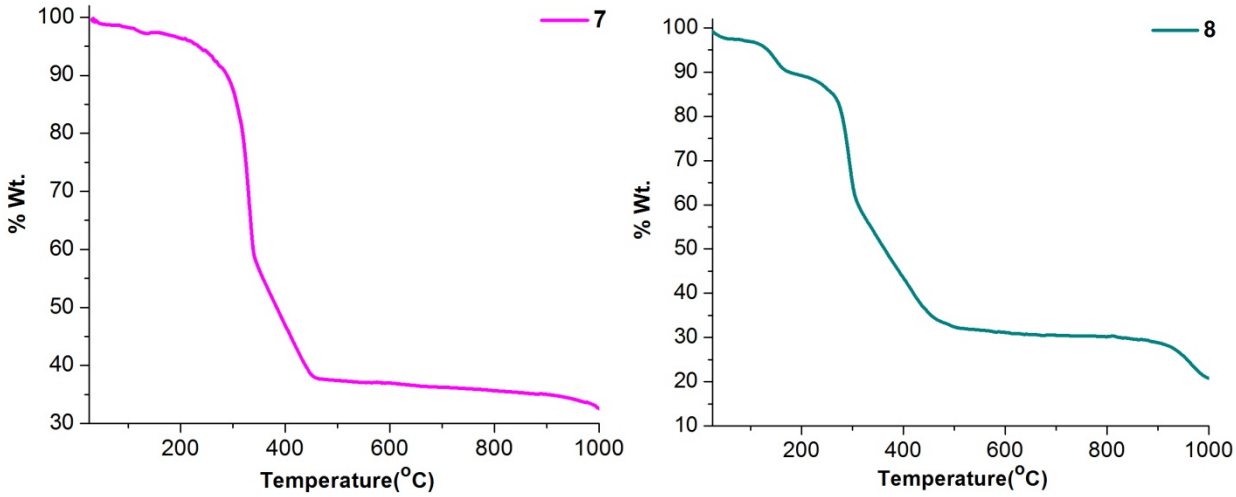

Figure S3. Thermogravimetric Analysis of compound **7** and **8**.

X-ray structure analysis

Intensity data were collected on an Oxford Xcalibur CCD diffractometer (**1**, **3, 6** and **7**) using monochromatic MoKα radiation. Intensity data for compound **2**, **4, 5** and **8** was collected on a Rigaku Saturn724+ diffractometer using MoKα radiation. All calculations were carried out using the programs in WinGX module.[1]The structure was solved in each case by direct methods (SIR-92).[2] The final refinement of the structure was carried out using full least-squares methods on F^2 using SHELXL-97[3] and SHELXL-2013.[4] Due to poor diffraction data of compound **7**, the structure could not be refined to satisfactory value and hence the metric parameters of this compound are not described in detail.

Table S1: Details of X-ray diffraction data of compound **1-4**.

Compound	**1**	**2**	**3**	**4**
Empirical formula	$C_{44}H_{56}CoN_4O_8P_2$	$C_{25}H_{37}CoN_2O_7$ P	$C_{54}H_{74}Co_2N_4O_{14}P_2$	$C_{19}H_{29}CoN_4O_5P$
Fw	889.80	567.46	1182.97	483.36
Temp, [K]	133(2)	150(2) K	120(2)	150(2) K
Crystal system	Triclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$	Pbca
a, [Å]	9.3002(8)	12.313(3)	11.3601(5)	26.081(6)
b, [Å]	9.6080(8)	12.624(3)	23.5841(11)	18.290(4)
c, [Å]	13.0067(10)	18.217(5)	11.9974(5)	9.713(2)
α, [°]	82.120(6)	90	90	90
β, [°]	86.980(6)	92.911(4)	115.741(5)	90
γ, [°]	68.922(6)	90	90	90
V, [Å^3]	1074.2(2)	2828.0(12)	2895.3(2)	4633.3(18)
Z	1	4	2	8
D(calcd), [g/cm^3]	1.375	1.333	1.357	1.386
μ [mm^{-1}]	0.531	0.707	0.694	0.846
GOF	1.043	1.093	1.035	1.164
R1($I_0>2\sigma(I_0)$)	0.0271	0.0300	0.0330	0.0620
wR2 (all data)	0.0714	wR2 = 0.0780	0.0765	0.1428
largest hole and peak [e · Å^{-3}]	-0.331, 0.210	0.441 and -0.464	-0.298, 0.321	0.664 and -0.599

Table S2: Details of X-ray diffraction data of compound **5**, 6 and **8**.

Compound	**5**	**6**	**8**
Empirical formula	$C_{46}\ H_{74}\ Co_2\ N_8\ O_{10}\ P_2$	$C_{68}\ H_{92}\ Co_4\ N_8\ O_{16}\ P_4$	$C_{72}H_{84}Co_4N_{12}O_{16}P_4$
Fw	1078.93	1637.10	1733.14
Temp, [K]	150(2) K	123(2) K	150(2)K
Crystal system	Triclinic	Monoclinic	Tetragonal
Space group	$P\bar{1}$	C 2/c	P4/nnc
a, [Å]	9.2911(16)	29.3794(12)	18.037(3)
b, [Å]	11.821(3)	14.5450(4)	18.037(3)
c, [Å]	12.926(3)	19.9624(7)	30.914(5)
α, [°]	88.042(7)	90	90
β, [°]	78.263(7)	111.705(4)	90
γ, [°]	82.427(8)	90	90
V, [Å^3]	1377.8(5)	7925.6(5)	10057(3)
Z	1	4	4
D(calcd), [g/cm^3]	1.30	1.372	1.145
μ [mm^{-1}]	0.718	0.969	0.768
GOF	1.062	1.025	1.123
R1(I_0>2σ(I_0))	0.0302	0.0560	0.0705
wR2 (all data)	0.0794	0.0967	0.1960
largest hole and peak [e · Å^{-3}]	0.361 and -0.312	-0.539, 0.805	0.408 and -0.430

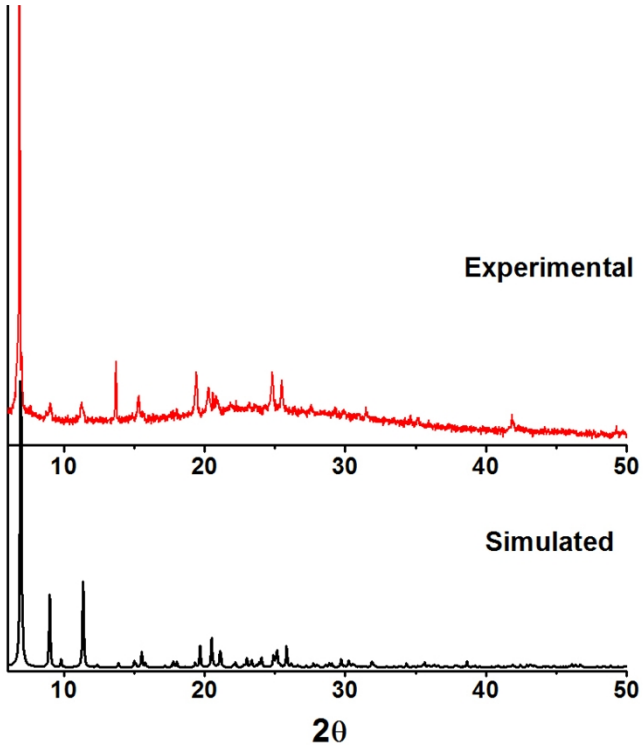

Figure S4. Simulated and experimental PXRD pattern of the activated compound **8**.

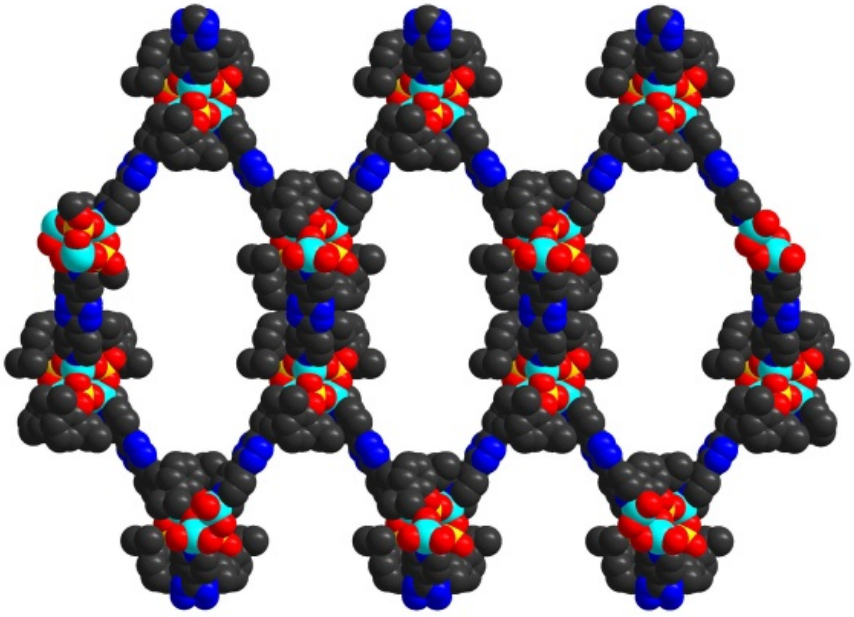

Figure S5. Space filling model showing hexagonal channels in the framework of **8**.

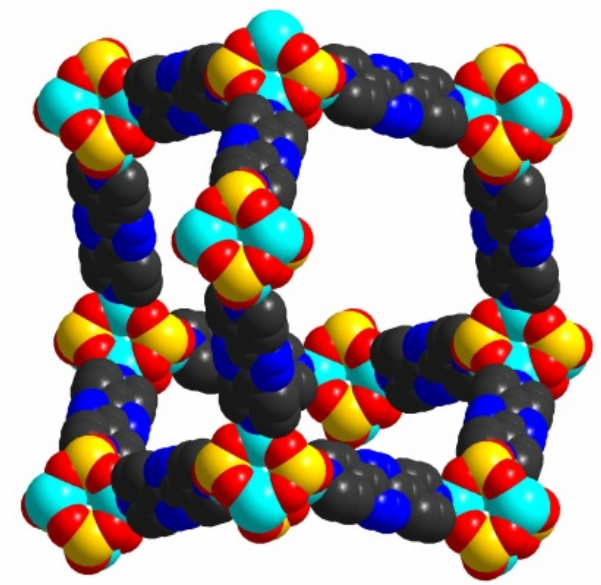

Figure S6. Space filling model showing a single unit of diamond framework in compound **8**.

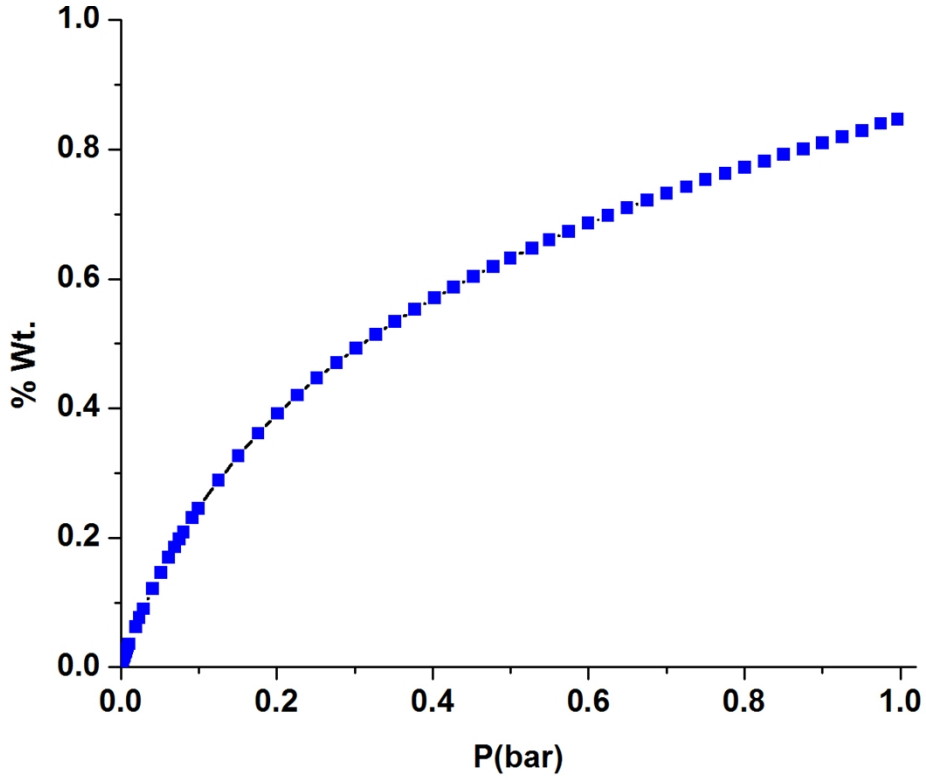

Figure S7. H_2 adsorption isotherm at 77K for framework **8**.

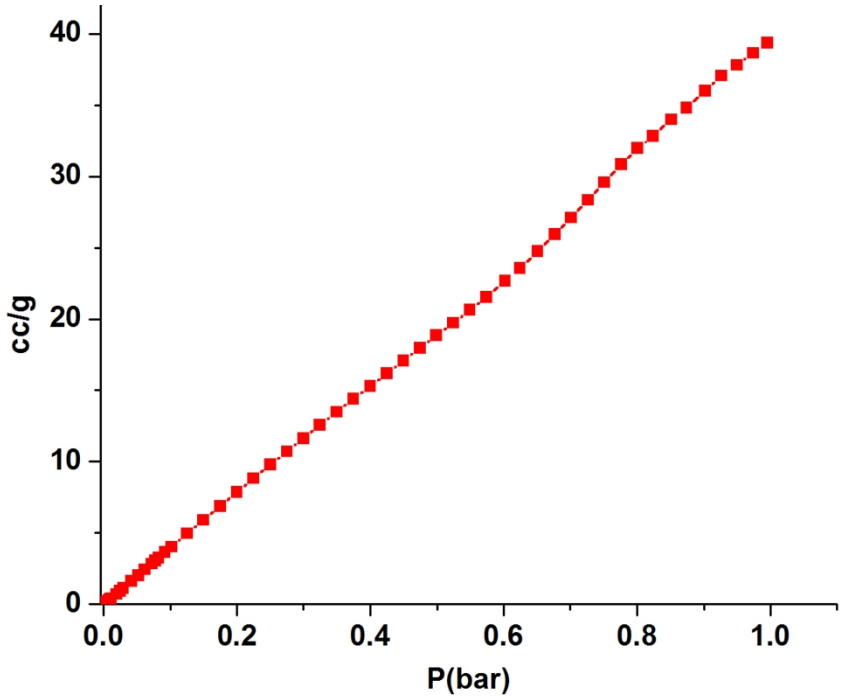

Figure S8. CO_2 adsorption isotherm at 273K for framework **8**.

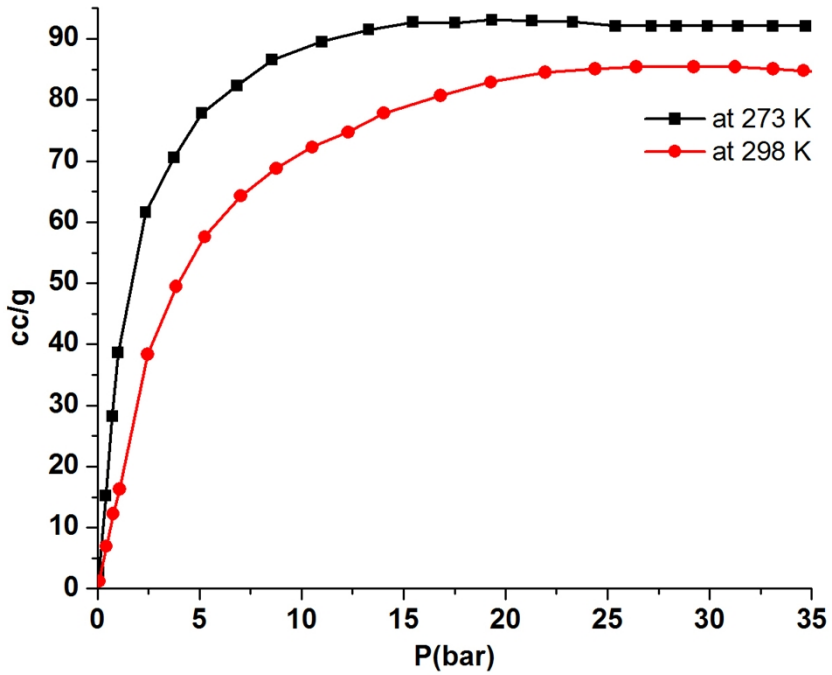

Figure S9. High pressure CO_2 adsorption isotherm at 273K and 298K for framework **8**.

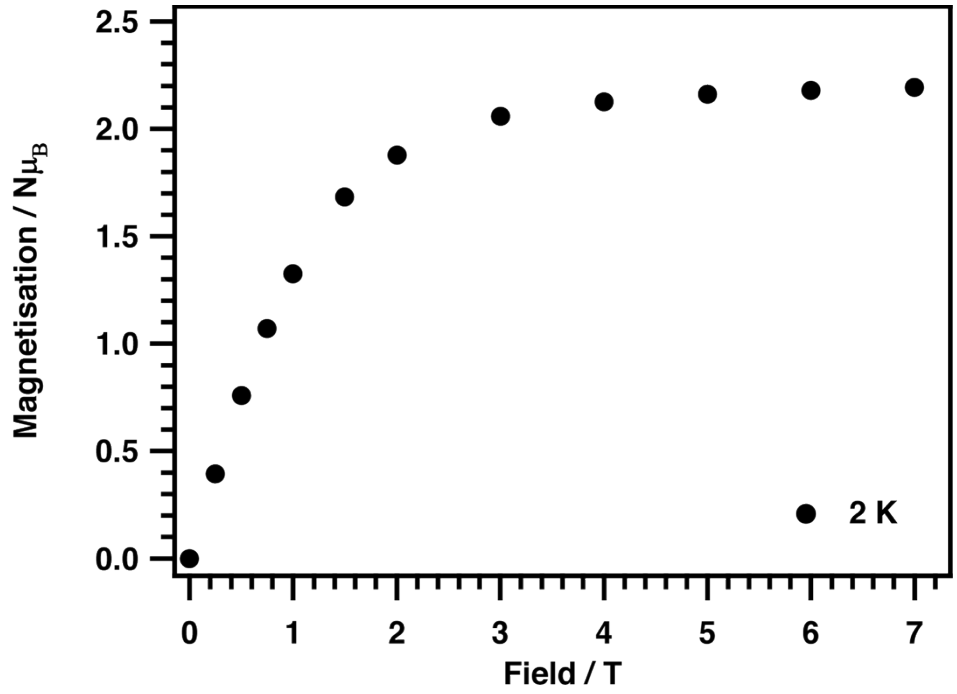

Figure S10: Field-dependent magnetisation of compound **1** at 2 K.

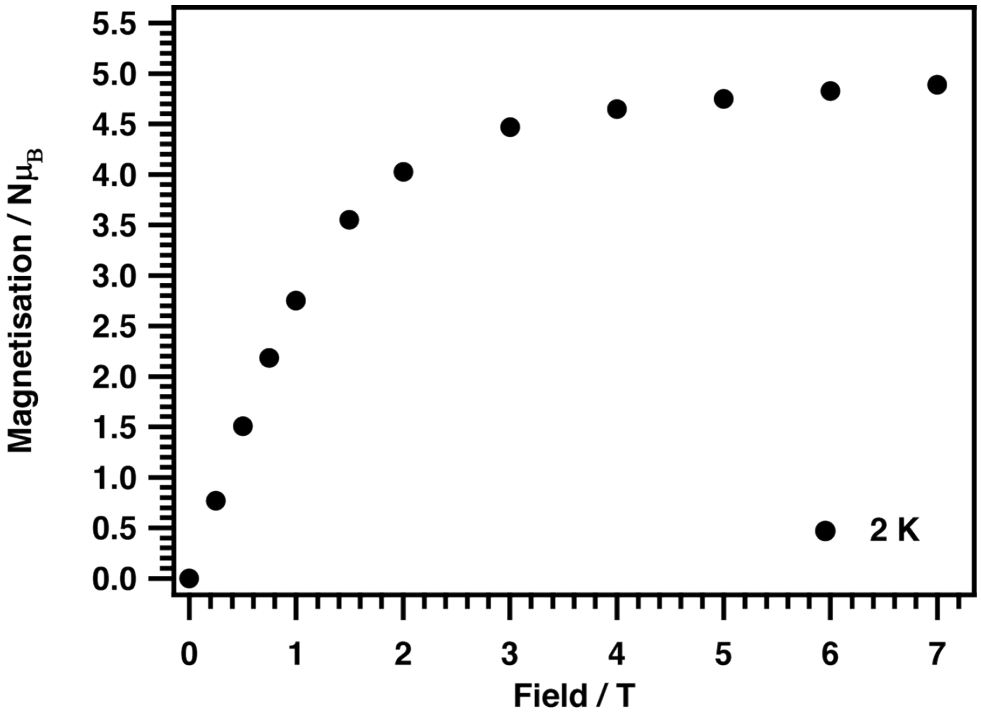

Figure S11: Field-dependent magnetisation of compound **3** at 2 K.

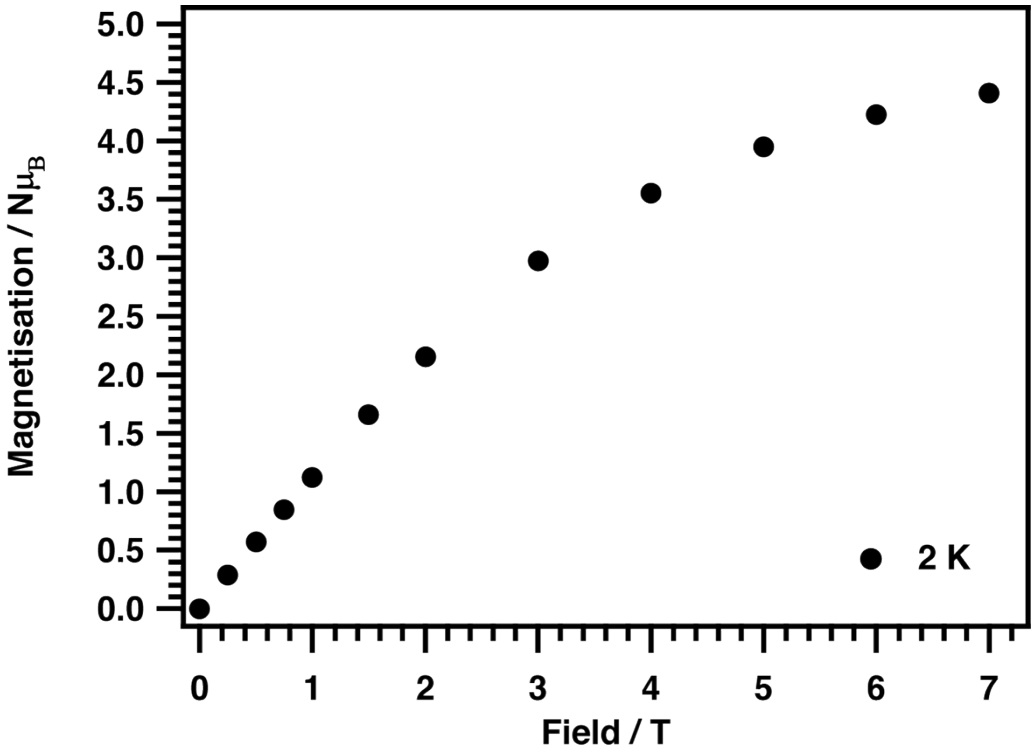

Figure S12: Field-dependent magnetisation of compound **2** at 2 K.

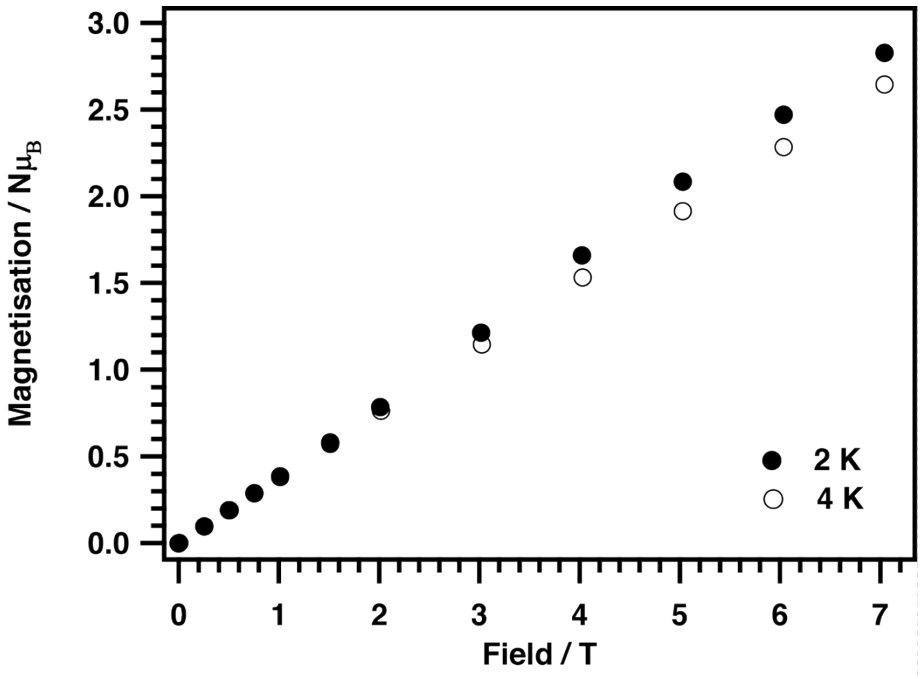

Figure S13: Field-dependent magnetisation of compound **4** at 2 and 4 K.

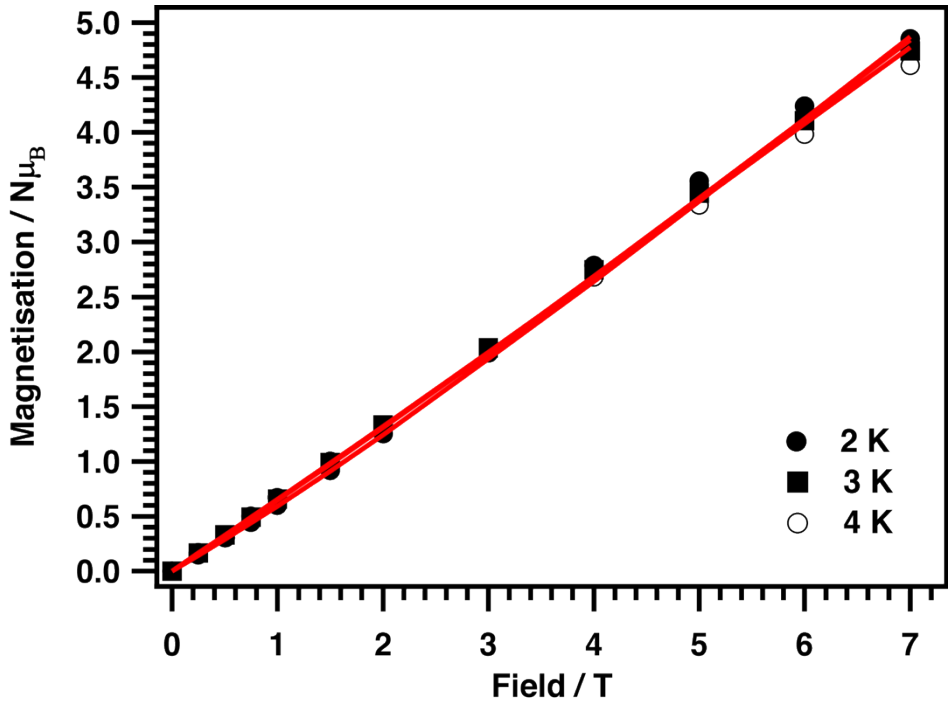

Figure S14: Field-dependent magnetisation of compound **6** at 2 and 4 K. Red lines represent calculations with $g = 2.36$, $J = -1.51$ cm^{-1}.

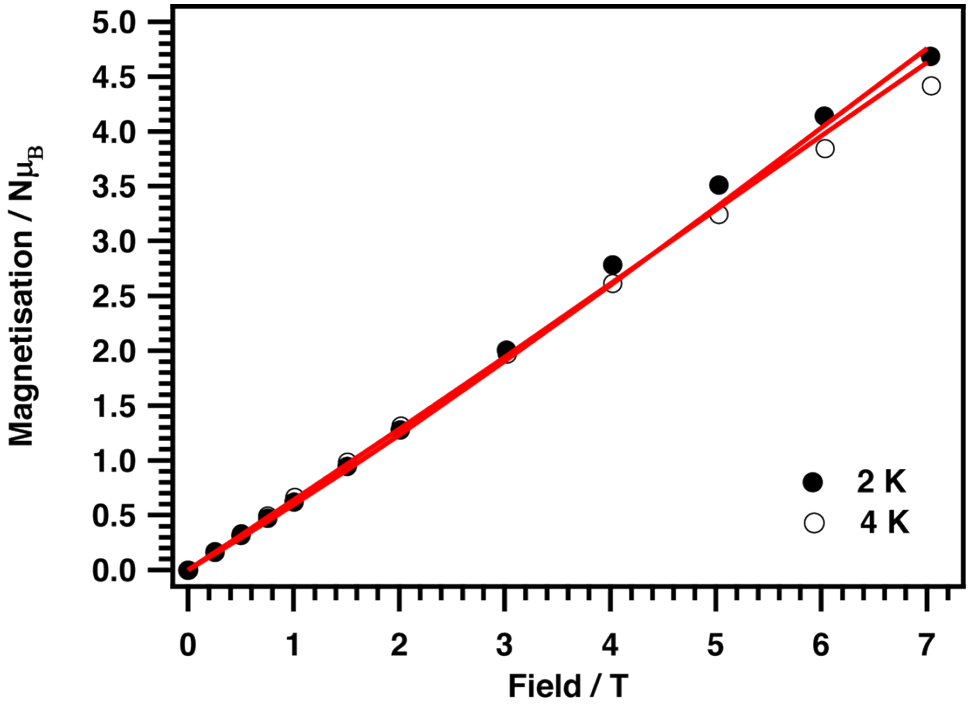

Figure S15: Field-dependent magnetisation of compound **7** at 2 and 4 K. Red lines represent calculation with $g = 2.23$, $J = -1.39$ cm^{-1}.

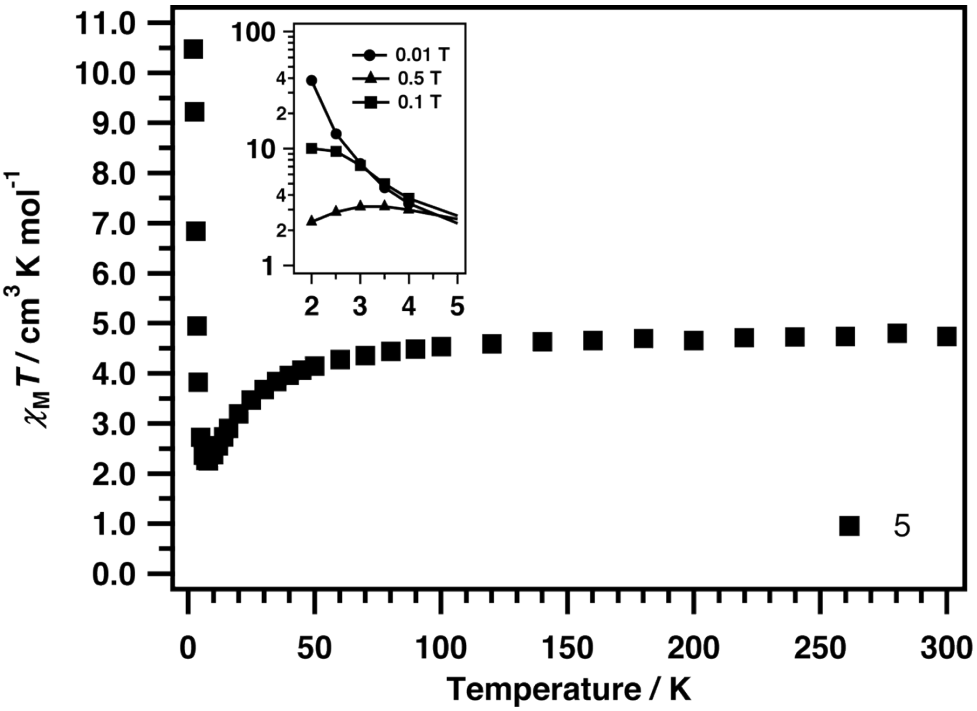

Figure S16: Temperature-dependent susceptibility of compound **5** under a static field of 0.1 T.

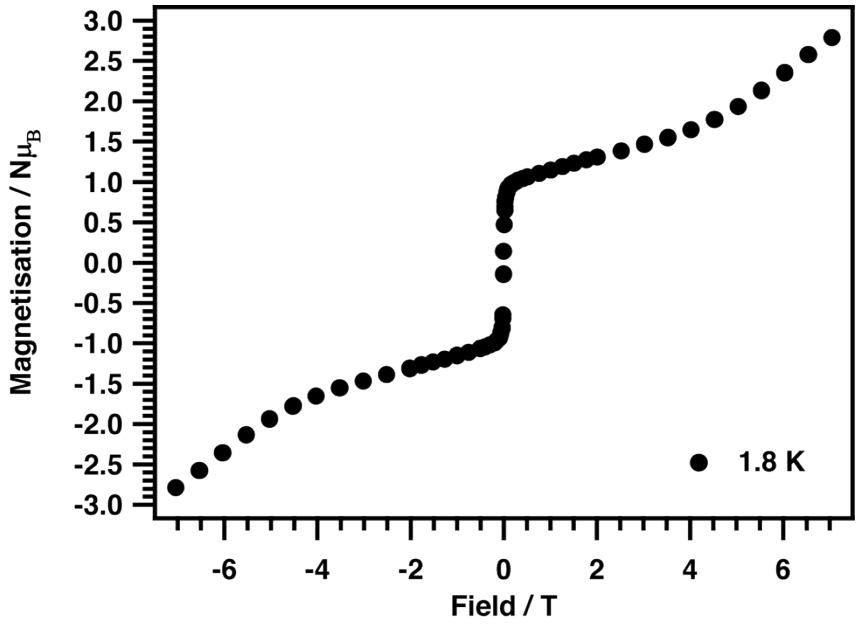

Figure S17: Field-dependent magnetisation of compound **5** at 1.8 K. The rise to ~1.1 Nμ_B between zero field and 0.3 T is not consistent with a simple isolated dimer. No hysteresis is observed.

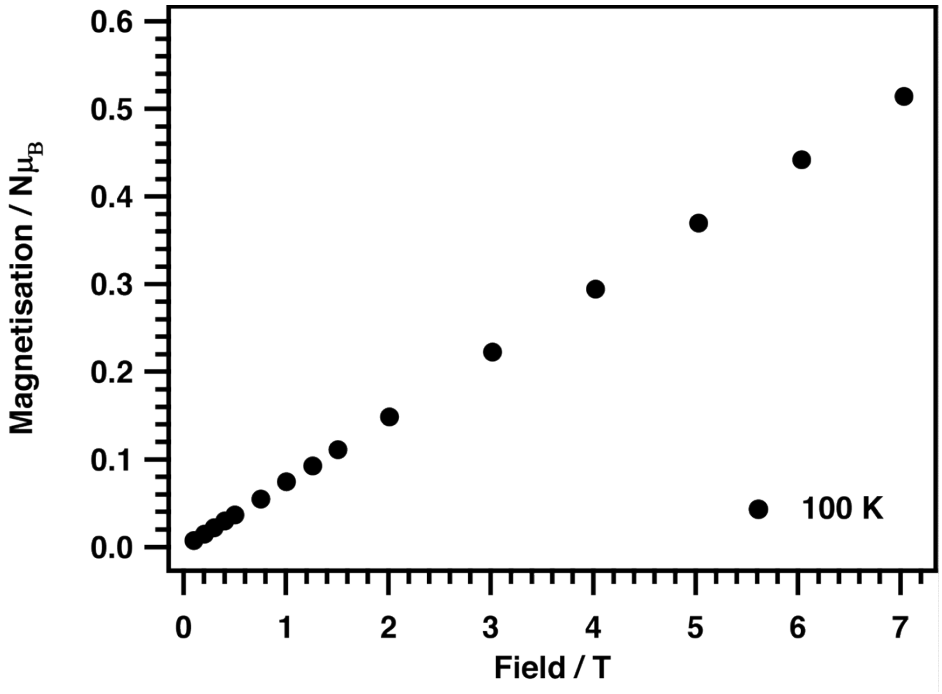

Figure S18: Field-dependent magnetisation measurements at 100 K show a linear increase with field: this appears to rule out the presence of common cobalt-oxide nanoparticles (e.g. Co_3O_4).

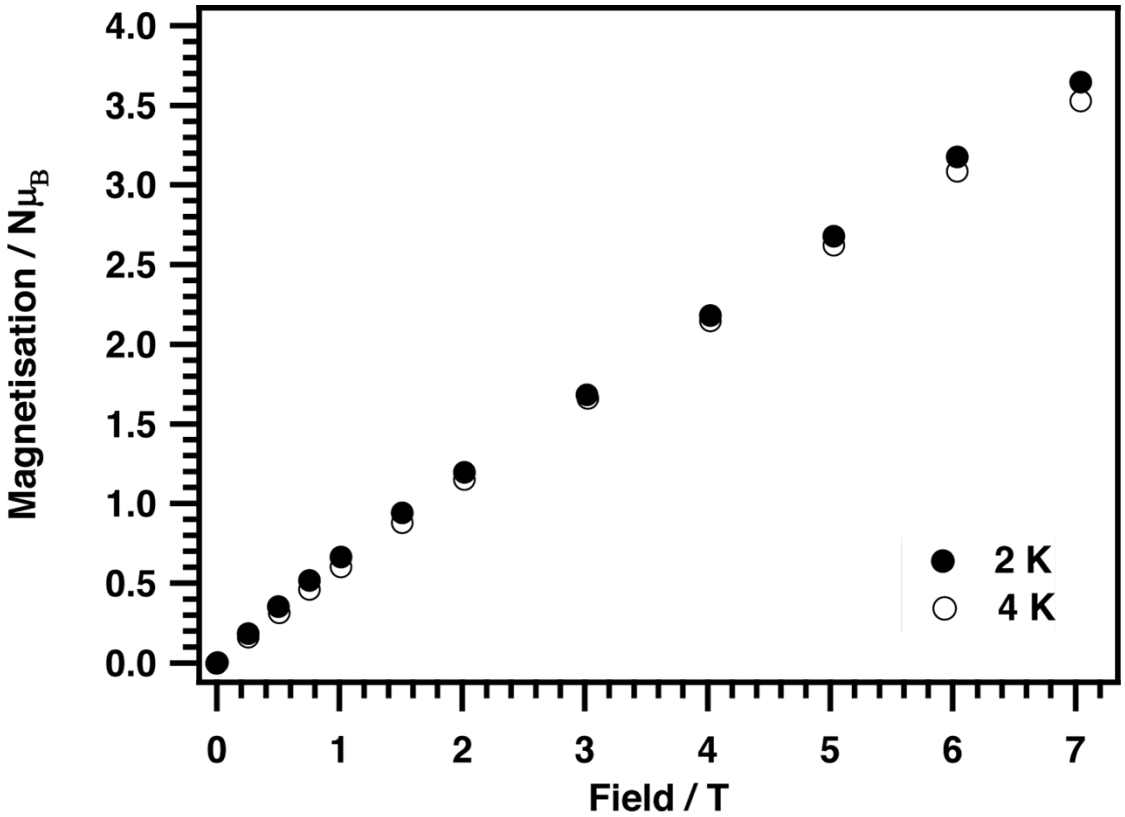

Figure S19: Field-dependent magnetisation of compound **8** at 2 and 4 K.

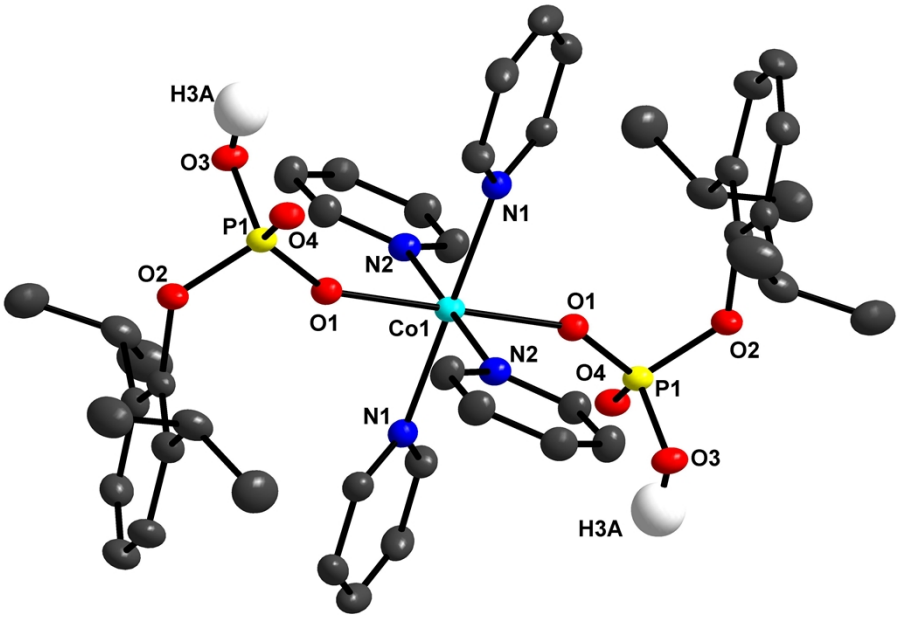

Figure S20. Thermal ellipsoid plot for $[Co(py)_4(dippH)_2]$ (**1**).

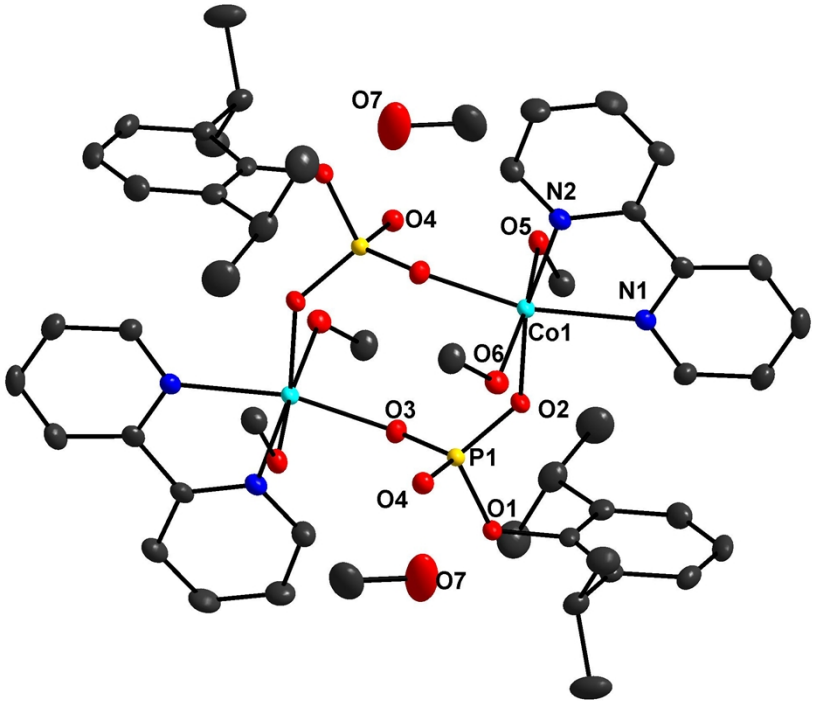

Figure S21. Thermal ellipsoid plot for $[Co(dipp)(bpy)(MeOH)_2]_2 \cdot 2MeOH$ (**2**).

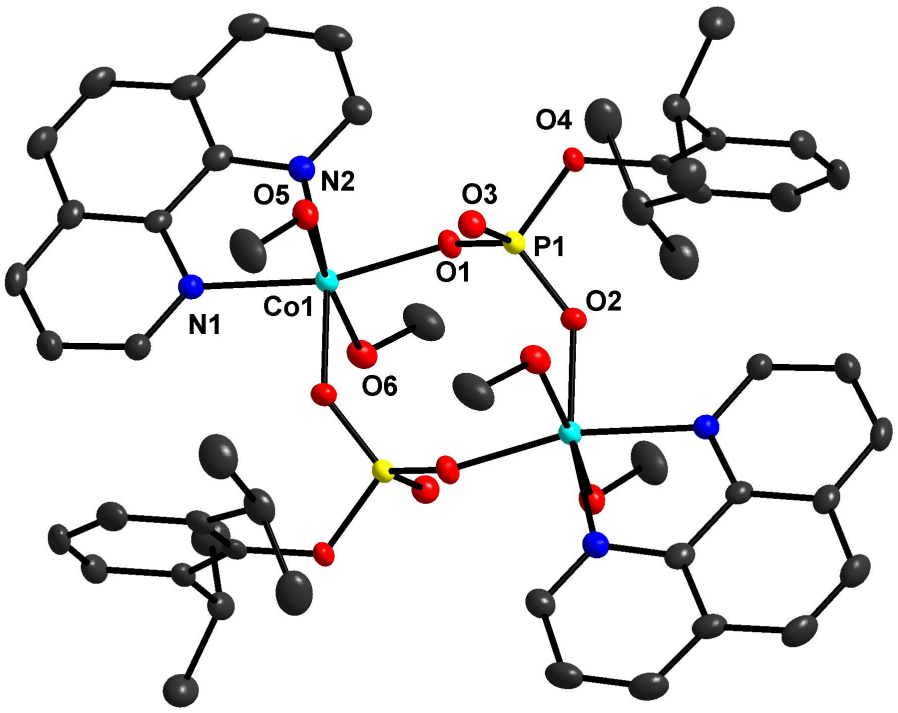

Figure S22. Thermal ellipsoid plot for $[Co(dipp)(phen)(MeOH)_2]_2 \cdot 2MeOH$ (**3**).

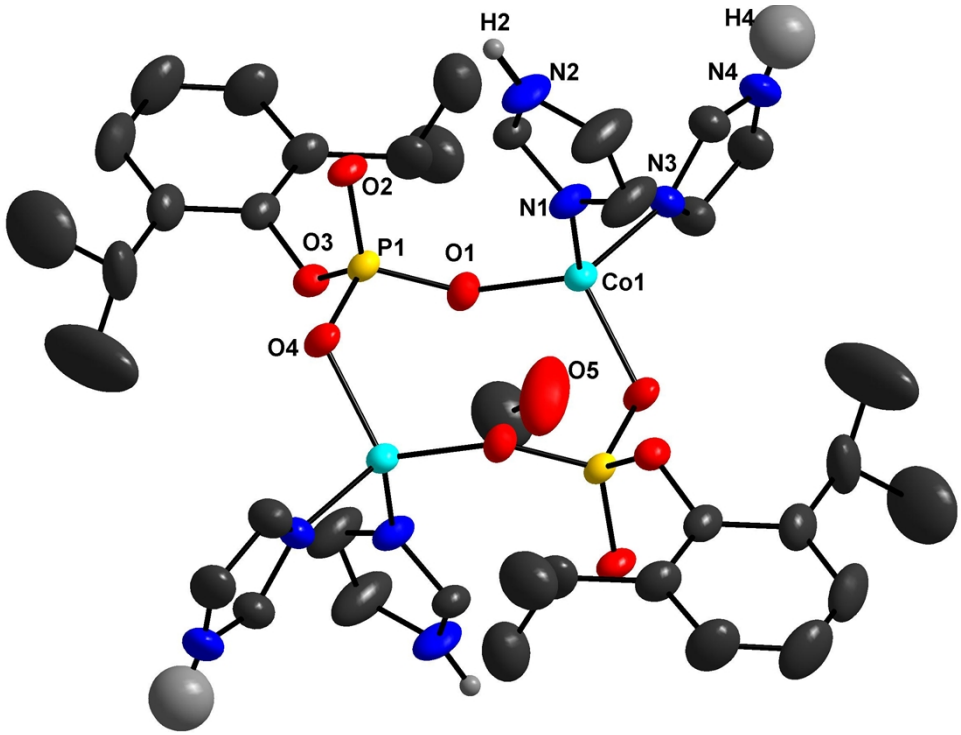

Figure S23. Thermal ellipsoid plot for $[Co(dipp)(Imz)_2]_2.2MeOH$ (**4**).

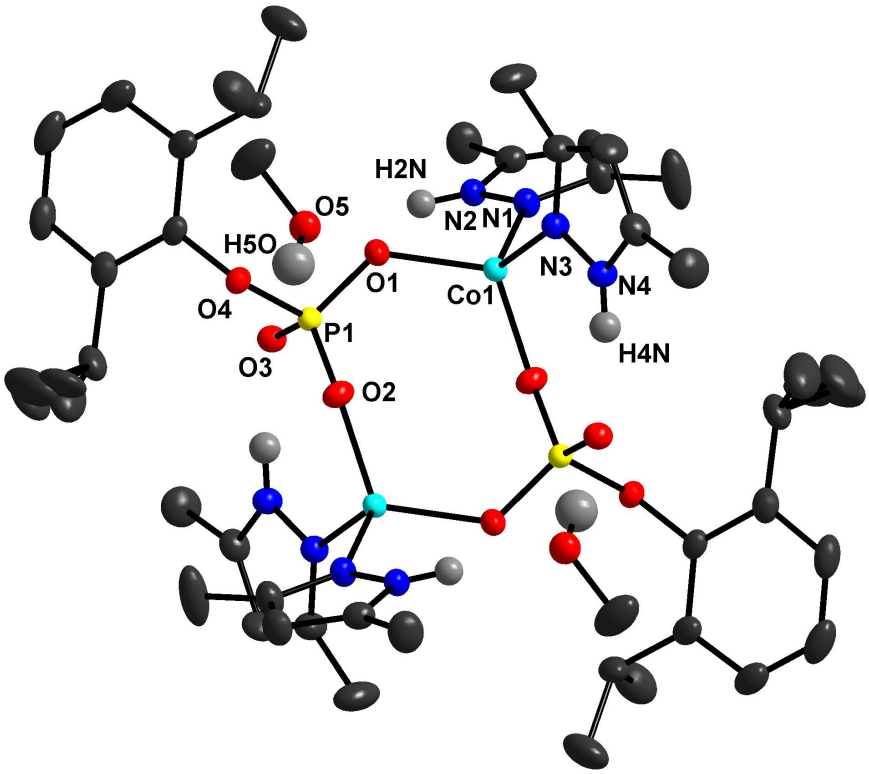

Figure S23. Thermal ellipsoid plot for $[Co(dmpz)_2(dipp)]_2.2MeOH$ (**5**).

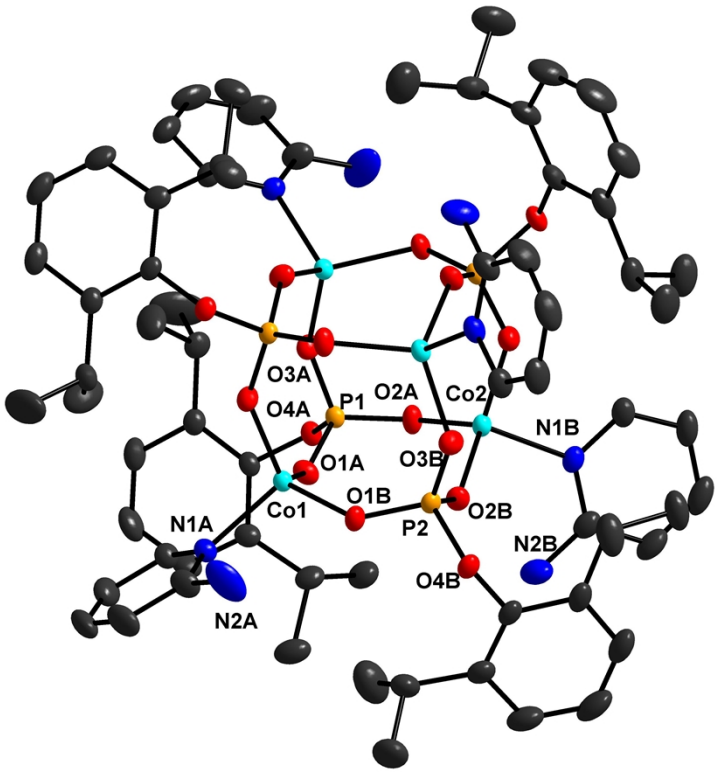

Figure S24. Thermal ellipsoid plot for $[Co(dipp)(2\text{-apy})]_4$ (**6**).

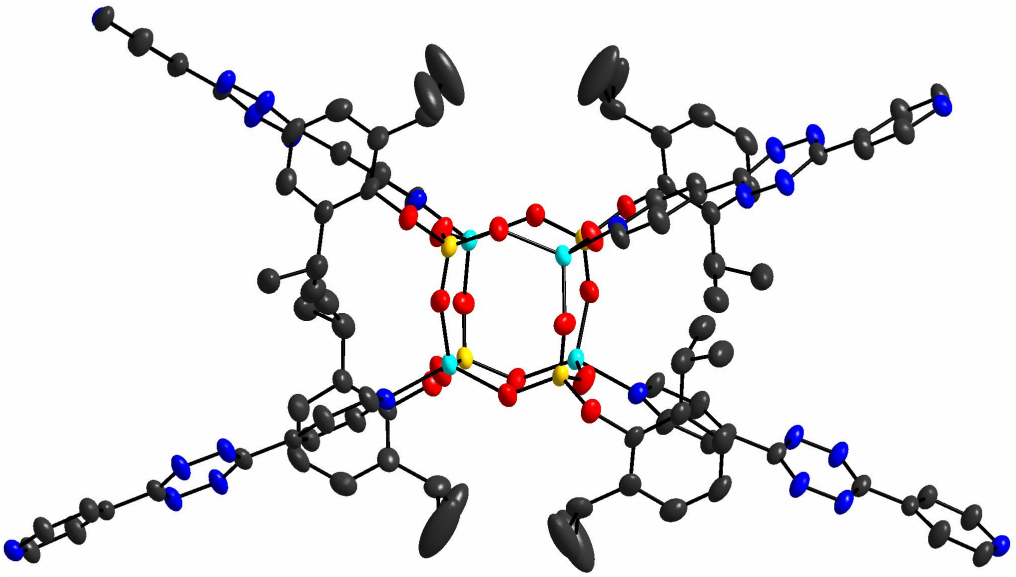

Figure S24. Thermal ellipsoid plot for $[Co(dipp)(dptz)]_{4n}$ (**8**).

Table S3. Selected bond lengths [Å] and angles [°] for $[Co(dippH)_2(py)_4]$ **(1)**

Co(1)-N(1)	2.150(1)	N(1)#1-Co(1)-N(1)	180.0	N(1)#1-Co(1)-N(2)	90.08(5)
Co(1)-O(1)	2.109(1)	N(1)-Co(1)-N(2)	89.92(5)	N(1)-Co(1)-N(2)#1	90.08(5)
P(1)-O(2)	1.615(1)	N(1)#1-Co(1)-N(2)#1	89.92(5)	N(2)-Co(1)-N(2)#1	180.0
P(1)-O(4)	1.496(1)	O(1)-Co(1)-N(1)	87.37(5)	O(1)#1-Co(1)-N(1)	92.63(5)
Co(1)-N(2)	2.232(1)	O(1)-Co(1)-N(1)#1	92.63(5)	O(1)#1-Co(1)-N(1)#1	87.37(5)
P(1)-O(1)	1.497(1)	O(1)-Co(1)-N(2)	91.51(5)	O(1)#1-Co(1)-N(2)	88.49(5)
P(1)-O(3)	1.567(1)	O(1)-Co(1)-N(2)#1	88.49(5)	O(1)#1-Co(1)-N(2)#1	91.51(5)
		O(1)-Co(1)-O(1)#1	180.0	O(1)-P(1)-O(2)	107.62(6)
		O(1)-P(1)-O(3)	111.03(7)	O(3)-P(1)-O(2)	101.04(7)
		O(4) -P(1)-O(1)	116.99(7)	O(4)-P(1)-O(2)	108.19(7)
		O(4)-P(1)-O(3)	110.66(7)	N(1)#1-Co(1)-N(2)	90.08(5)

Table S4. Selected bond lengths [Å] and angles [°] for $[Co(dipp)(bpy)(MeOH)_2]_2.2MeOH$ (**2**)

Co(1)-O(2)	1.9967(11)	O(2)-Co(1)-O(3)#1	104.30(5)	N(2)-Co(1)-O(6)	93.36(5)
Co(1)-O(3)#1	2.0094(11)	O(2)-Co(1)-N(2)	165.08(5)	N(1)-Co(1)-O(6)	97.78(5)
Co(1)-N(2)	2.1191(14)	O(3)#1-Co(1)-N(2)	90.18(5)	O(5)-Co(1)-O(6)	170.75(4)
Co(1)-N(1)	2.1547(14)	O(2)-Co(1)-N(1)	89.94(5)	O(3)-P(1)-O(2)	114.22(6)
Co(1)-O(5)	2.2301(12)	O(3)#1-Co(1)-N(1)	165.57(5)	O(3)-P(1)-O(4)	112.12(6)
Co(1)-O(6)	2.2307(12)	N(2)-Co(1)-N(1)	75.76(5)	O(2)-P(1)-O(4)	112.82(6)
P(1)-O(3)	1.5109(12)	O(2)-Co(1)-O(5)	90.07(5)	O(3)-P(1)-O(1)	103.83(6)
P(1)-O(2)	1.5176(12)	O(3)#1-Co(1)-O(5)	88.21(5)	O(2)-P(1)-O(1)	105.40(6)
P(1)-O(4)	1.5280(12)	N(1)-Co(1)-O(5)	89.48(5)	O(4)-P(1)-O(1)	107.58(6)
P(1)-O(1)	1.6329(11)	O(2)-Co(1)-O(6)	84.24(5)	P(1)-O(2)-Co(1)	129.98(7)
		O(3)#1-Co(1)-O(6)	86.14(5)	P(1)-O(3)-Co(1)#1	137.49(7)

Table S5. Selected bond lengths [Å] and angles [°] for [Co)(dipp)(phen)$(MeOH)_2$].2MeOH **(3)**

Co(1)-N(1)	2.1418(2)	N(1)-Co(1)-N(2)	76.72(7)	O(1)-Co(1)-O(5)	86.17(6)
Co(1)-N(2)	2.1517(2)	N(1)-Co(1)-O(1)	165.51(7)	O(1)-Co(1)-O(6)	89.12(7)
Co(1)-O(1)	2.0023(1)	N(1)-Co(1)-O(2)	90.44(7)	O(2)-Co(1)-O(5)	89.72(6)
Co(1)-O(2)	2.0139(1)	N(1)-Co(1)-O(5)	90.00(7)	O(2)-Co(1)-O(6)	86.15(6)
Co(1)-O(5)	2.1990(2)	N(1)-Co(1)-O(6)	95.86(7)	O(5)-Co(1)-O(6)	172.85(7)
Co(1)-O(6)	2.1810(2)	N(2)-Co(1)-O(1)	89.63(7)	P(1)-O(1)-Co(1)	134.96(9)
P(1)-O(1)	1.502(1)	N(2)-Co(1)-O(2)	166.49(7)	P(2)-O(2)-Co(1)	133.76(0)
P(1)-O(2)	1.512(2)	N(2)-Co(1)-O(5)	94.41(7)		
P(1)-O(3)	1.5241(2)	N(2)-Co(1)-O(6)	90.93(7)		
P(1)-O(4)	1.6262(1)	O(1)-Co(1)-O(2)	103.49(6)		

Table S6. Selected bond lengths [Å] and angles [°] for $[Co(Imz)_2(dipp)]_2.2MeOH$ **(4)**

Co(1)-O(1)	1.936(3)	O(1)-Co(1)-O(4)	111.67(12)	P(1)#1-O(4)-Co(1)	122.07(15)
Co(1)-O(4)	1.946(3)	O(1)-Co(1)-N(1)	112.76(13)	O(2)-P(1)-O(1)	116.07(17)
Co(1)-N(1)	2.009(3)	O(4)-Co(1)-N(1)	112.03(13)	O(2)-P(1)-O(4)#1	113.12(17)
Co(1)-N(3)	2.009(3)	O(1)-Co(1)-N(3)	109.70(13)	O(1)-P(1)-O(4)#1	109.17(15)
O(1)-P(1)	1.524(3)	O(4)-Co(1)-N(3)	106.40(13)	O(2)-P(1)-O(3)	109.30(15)
O(2)-P(1)	1.483(3)	N(1)-Co(1)-N(3)	103.77(15)	O(1)-P(1)-O(3)	103.57(15)
O(3)-P(1)	1.613(3)	P(1)-O(1)-Co(1)	135.10(17)	O(4)#1-P(1)-O(3)	104.55(16)
O(4)-P(1)#1	1.531(3)				

Table S7. Selected bond lengths [Å] and angles [°] for $[Co(dipp)(dmpz)_2]_2.2MeOH$ **(5)**

Co(1)-O(2)#1	1.9197(13)	O(2)#1-Co(1)-O(1)	116.49(6)
Co(1)-O(1)	1.9255(13)	O(2)#1-Co(1)-N(3)	109.96(6)
Co(1)-N(3)	2.0079(15)	O(1)-Co(1)-N(3)	111.87(6)
Co(1)-N(1)	2.0155(16)	O(2)#1-Co(1)-N(1)	104.76(6)
P(1)-O(3)	1.5073(13)	O(1)-Co(1)-N(1)	103.20(6)
P(1)-O(2)	1.5157(13)	N(3)-Co(1)-N(1)	109.96(6)
P(1)-O(1)	1.5220(13)	P(1)-O(1)-Co(1)	127.42(8)
P(1)-O(4)	1.6219(13)	P(1)-O(2)-Co(1)#1	137.11(8)

Table S8. Selected bond lengths [Å] and angles [°] for $[Co(dipp)(2\text{-apy})]_4$ (**6**)

Co(1)-O(3A)#1	1.9210(14)	O(3A)#1-Co(1)-O(1A)	114.05(6)	P(2)-O(1B)-Co(1)	128.06(9)
Co(1)-O(1A)	1.9282(13)	O(3A)#1-Co(1)-O(1B)	109.62(6)	P(2)-O(2B)-Co(2)	135.44(10)
Co(1)-O(1B)	1.9531(14)	O(1A)-Co(1)-O(1B)	115.02(6)	P(2)-O(3B)-Co(2)#1	138.62(10)
Co(1)-N(1A)	2.0333(17)	O(3A)#1-Co(1)-N(1A)	107.42(7)	O(3A)-P(1)-O(1A)	112.97(8)
Co(2)-O(2A)	1.9205(14)	O(1A)-Co(1)-N(1A)	102.65(6)	O(3A)-P(1)-O(2A)	113.63(9)
Co(2)-O(3B)#1	1.9224(16)	O(1B)-Co(1)-N(1A)	107.38(7)	O(1A)-P(1)-O(2A)	114.36(9)
Co(2)-O(2B)	1.9407(14)	O(2A)-Co(2)-O(3B)#1	114.03(7)	O(3A)-P(1)-O(4A)	107.19(8)
Co(2)-N(1B)	2.0453(17)	O(2A)-Co(2)-O(2B)	108.24(6)	O(1A)-P(1)-O(4A)	106.90(8)
P(1)-O(3A)	1.5052(15)	O(3B)#1-Co(2)-O(2B)	118.89(6)	O(2A)-P(1)-O(4A)	100.51(7)
P(1)-O(1A)	1.5114(14)	O(2A)-Co(2)-N(1B)	113.00(7)	O(3B)-P(2)-O(1B)	113.43(9)
P(1)-O(2A)	1.5211(15)	O(3B)#1-Co(2)-N(1B)	100.46(7)	O(3B)-P(2)-O(2B)	113.39(9)
P(1)-O(4A)	1.6132(14)	O(2B)-Co(2)-N(1B)	101.31(7)	O(1B)-P(2)-O(2B)	112.29(8)
P(2)-O(3B)	1.5097(16)	P(1)-O(1A)-Co(1)	135.79(9)	O(3B)-P(2)-O(4B)	103.98(8)
P(2)-O(1B)	1.5177(15)	P(1)-O(2A)-Co(2)	129.40(9)	O(1B)-P(2)-O(4B)	106.28(8)
P(2)-O(2B)	1.5188(15)	P(1)-O(3A)-Co(1)#1	143.15(9)	O(2B)-P(2)-O(4B)	106.59(8)
P(2)-O(4B)	1.6070(14)				

Table S9. Selected bond lengths [Å] and angles [°] for $[Co_4(dipp)_4(2\text{-apy})_3(DMSO)]\cdot(DMSO)\cdot(H_2O)$ (**7**)

Co(1)-O(5)	1.924(13)	Co(4)-O(11)	1.890(13)	O(2)-Co(2)-N(1)	107.9(6)
Co(1)-O(1)	1.940(11)	Co(4)-O(15)	1.939(10)	O(13)-Co(2)-N(1)	103.2(6)
Co(1)-O(17)	1.960(12)	Co(4)-N(5)	2.036(11)	O(10)-Co(3)-O(14)	113.5(6)
Co(1)-O(9)	1.966(9)	O(5)-Co(1)-O(1)	111.4(5)	O(10)-Co(3)-O(3)	111.4(5)
Co(2)-O(6)	1.903(12)	O(5)-Co(1)-O(17)	100.7(6)	O(14)-Co(3)-O(3)	116.9(5)
Co(2)-O(2)	1.921(13)	O(1)-Co(1)-O(17)	102.6(6)	O(10)-Co(3)-N(3)	101.4(5)
Co(2)-O(13)	1.921(11)	O(5)-Co(1)-O(9)	118.4(5)	O(14)-Co(3)-N(3)	105.7(6)
Co(2)-N(1)	2.014(14)	O(1)-Co(1)-O(9)	114.9(5)	O(3)-Co(3)-N(3)	106.1(6)
Co(3)-O(10)	1.916(12)	O(17)-Co(1)-O(9)	106.1(5)	O(7)-Co(4)-O(11)	115.0(6)
Co(3)-O(14)	1.932(13)	O(6)-Co(2)-O(2)	107.8(5)	O(7)-Co(4)-O(15)	114.2(5)
Co(3)-O(3)	1.947(11)	O(6)-Co(2)-O(13)	113.4(5)	O(11)-Co(4)-O(15)	113.5(6)
Co(3)-N(3)	2.030(13)	O(2)-Co(2)-O(13)	118.6(5)	O(7)-Co(4)-N(5)	103.7(5)
Co(4)-O(7)	1.883(13)	O(6)-Co(2)-N(1)	104.8(6)		

Table S10. Selected bond lengths [Å] and angles [°] for $\{[Co(dipp)(dptz)_{0.5}]_4\}_n$ (**8**)

Co(1)-O(1)	1.914(3)	O(1)-Co(1)-O(2)	108.12(13)	O(2)#2-P(1)-O(1)	111.98(17)
Co(1)-O(2)	1.917(3)	O(1)-Co(1)-O(3)	116.89(14)	O(3)#1-P(1)-O(4)	107.25(17)
Co(1)-O(3)	1.925(3)	O(2)-Co(1)-O(3)	120.58(15)	O(2)#2-P(1)-O(4)	104.92(16)
Co(1)-N(1)	2.026(3)	O(1)-Co(1)-N(1)	112.45(14)	O(1)-P(1)-O(4)	104.31(17)
P(1)-O(3)#1	1.497(3)	O(2)-Co(1)-N(1)	100.28(13)	P(1)-O(1)-Co(1)	126.38(19)
P(1)-O(2)#2	1.509(3)	O(3)-Co(1)-N(1)	96.42(13)	P(1)#2-O(2)-Co(1)	139.2(2)
P(1)-O(1)	1.517(3)	O(3)#1-P(1)-O(2)#2	113.6(2)	P(1)#1-O(3)-Co(1)	141.50(19)
P(1)-O(4)	1.608(3)	O(3)#1-P(1)-O(1)	113.75(18)	O(2)#2-P(1)-O(1)	111.98(17)

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