

Electronic Supplementary Information (ESI)

Isomorphic Co(II) and Zn(II) Phosphonates: Co-Crystal formation of $[\{M_2(\eta^1\text{-DMPzH})_4(\text{Cl}_3\text{CPO}_3)_2\}\{M(\eta^1\text{-DMPzH})_2\text{Cl}_2\}_2](\text{toluene})_2$ (M = Co(II) and Zn(II))

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EXPERIMENTAL SECTION:

Reagents and General Procedures:

Solvents and other general reagents used in this work were purified according to standard procedures. Following chemicals were used as obtained. Anhydrous ZnCl₂ (Lancaster, U. K.), Anhydrous CoCl₂ (Lancaster, U. K.), AlCl₃ (S. D. Fine Chemicals, India), PCl₃ (S. D. Fine Chemicals, India), 2,4-Pentanedione (S. D. Fine Chemicals, India), and hydrazine hydrate (N₂H₄·H₂O; S. D. Fine Chemicals, India), acetonitrile (S. D. Fine Chemicals, India), methanol (S. D. Fine Chemicals, India), triethylamine (S. D. Fine Chemicals, India) were used as received. (trichloromethyl)phosphonic acid (Cl₃CPO₃H₂)^{S1} and 3,5-dimethyl-1*H*-pyrazole^{S2} were prepared by following the published procedures.

Synthesis:

Synthesis of 1 (Scheme 1a): Anhydrous CoCl₂ (0.0396 g, 0.305 mmol) was taken in acetonitrile (25 mL). To this a solution of 3,5-dimethyl-1*H*-pyrazole (0.0293 g, 0.305 mmol) and (trichloromethyl)phosphonic acid (0.0304 g, 0.152 mmol) in acetonitrile (15 mL) were added, and the resulting mixture was stirred at room temperature for 24 h. At this stage, triethylamine (0.0622 g, 0.610 mmol) was added to the reaction mixture. The resulting clear colorless solution was stirred for an additional 24 h. The solution was evaporated, and the residue obtained was redissolved in toluene and kept for crystallization by vapor diffusion method with hexane. After 5-6 days, purple block-shaped crystals of **1** were obtained. Yield: 0.055 g, 41.16% (based on cobalt). C, H, N analysis: Anal. calcd. for C₅₆H₈₀Cl₁₀N₁₆O₆P₂Co₄ (**1**): C 38.98, H 4.67, N 12.99, Found: C 38.95, H 4.64, N 12.97. Mp. ~110 °C (d). ESI-HRMS (m/z): 914.79 [Co₂(η¹-

$\text{DMPzH}_4(\text{Cl}_3\text{CPO}_3)_2\} + \text{H}_2\text{O} + \text{H}^+]^+$. IR (KBr, ν/cm^{-1}): 2854 (b), 1595(m), 1425(m), 1311(m), 1136(s), 1116(s), 1033(s), 1053(s), 808(m), 761(s), 559(s), 426(s).

Synthesis of 2 (Scheme 1b): Anhydrous ZnCl_2 (0.0416 g, 0.305 mmol) was taken in acetonitrile (25 mL). To this a solution of 3,5-dimethyl-1*H*-pyrazole (0.0293 g, 0.0305 mmol) and (trichloromethyl)phosphonic acid (0.0304 g, 0.152 mmol) in acetonitrile (25 mL) were added and the resulting mixture was stirred at room temperature for 24 h. At this stage, triethylamine (0.0622 g, 0.610 mmol) was added to the reaction mixture. The resulting clear colorless solution was stirred for an additional 24 h. The solution was evaporated and the residue obtained was redissolved in toluene, and kept for crystallization by vapor diffusion method with hexane. After 5-6 days colorless block shaped crystals of **2** were obtained. Yield: 0.051 g, 38.19% (based on zinc). C, H, N analysis: Anal. calcd. for $\text{C}_{56}\text{H}_{80}\text{Cl}_{10}\text{N}_{16}\text{O}_6\text{P}_2\text{Zn}_4$ (**2**) C, 38.40; H, 4.60; N, 12.80, Found: C 38.39, H 4.57, N 12.86. Mp. ~ 125 °C (d). ESI-HRMS (m/z): 960.60 [$\{\text{Zn}_2(\eta^1\text{-DMPzH}_4(\text{Cl}_3\text{CPO}_3)_2\} + \text{H}_2\text{O} + \text{CH}_3\text{OH} + \text{H}^+]^+$ IR (KBr, ν/cm^{-1}): 3338 (b), 2927 (m), 2855 (m), 1598 (m), 1573 (m), 1385 (m), 1314 (w), 1165 (s), 1040 (s), 815 (w), 762 (s), 737 (s), 672 (w), 563 (s), 467 (w), 426 (m). ^1H NMR (500 MHz, DMSO-d_6): δ 7.09-7.22 (Ar-5H), δ 2.26 [(CH₃, Tol), δ 2.08 [(CH₃, Pz), s], δ 5.70 [(CH, Pz), s], ^{31}P NMR (500 MHz, DMSO-d_6): δ 3.18(s).

Synthesis of 3 (Scheme 2a): Anhydrous CoCl_2 (0.0475 g, 0.366 mmol) was taken in methanol (25 mL). To this a solution of 3,5-dimethyl-1*H*-pyrazole (0.0352 g, 0.366 mmol) and (trichloromethyl)phosphonic acid (0.0365 g, 0.183 mmol) in methanol (25 mL) were added and the resulting mixture was stirred at room temperature for 24 h. At this stage, triethylamine (0.0746 g, 0.732 mmol) was added to the reaction mixture. The resulting clear colorless solution was stirred for an additional 24 h. The solution was evaporated, and the residue obtained was

redissolved in toluene, and kept for crystallization by vapor diffusion method with hexane. After 4-5 days purple block shaped crystals of **3** were obtained. Yield: 0.066 g, 36.32% (based on cobalt). C, H, N analysis: Anal. calcd. for $C_{24}H_{48}Cl_8N_6O_6P_2Co_2$ (**3**) C, 29.41; H, 4.94; N, 8.57, Found: C, 29.40; H, 4.91; N, 8.59. Mp. $\sim 115^\circ C$ (d). ESI-HRMS (m/z): 778.59 [$\{Co_2(\eta^1-DMPzH)_2Cl_2(Cl_3CPO_3)_2\} + 3H^+\}^+$]. IR (KBr, v/cm^{-1}): 3349 (b), 2930 (s), 2678 (s), 2493 (s), 1570 (m), 1476 (s), 1398 (m), 1310 (m), 1117 (s), 1035 (s), 807 (m), 753 (m), 558 (s), 427 (m).

Synthesis of 4 (Scheme 2b): Anhydrous $ZnCl_2$ (0.0499 g, 0.366 mmol) was taken in methanol (25 mL). To this a solution of 3,5-dimethyl-1H-pyrazole (0.035 g, 0.366 mmol) and (trichloromethyl)phosphonic acid (0.0365 g, 0.183 mmol) in methanol (25 mL) were added and the resulting mixture was stirred at room temperature for 24 h. At this stage, triethylamine (0.0746 g, 0.732 mmol) was added to the reaction mixture. The resulting clear colorless solution was stirred for an additional 24 h. The solution was evaporated, and the residue obtained was redissolved in toluene, and kept for crystallization by vapor diffusion method with hexane. After 3-4 days colorless block shaped of crystals of **4** were obtained. Yield: 0.070 g, 39.03 % (based on zinc). C, H, N analysis: Anal. calcd. for $C_{24}H_{48}Cl_8Zn_2N_6O_6P_2$ (**4**) C, 29.03; H, 4.87; N, 9.67, Found: C, 29.39; H, 4.92; N, 8.59. Mp. $\sim 125^\circ C$ (d). ESI-HRMS (m/z): 790.84 [$\{Zn_2(\eta^1-DMPzH)_2Cl_2(Cl_3CPO_3)_2\} + 3H^+\}^+$]. IR (KBr, v/cm^{-1}): 3276 (w), 2985 (m), 2928 (m), 2852 (w), 2483 (w), 1593 (w), 1480 (m), 1310 (m), 1121(s), 1170 (s), 1049 (m), 1019 (s), 808 (m), 755 (s), 549 (s), 427 (w). 1H NMR (500 MHz, $DMSO-d_6$): δ 1.13 [$N(CH_2CH_3)_3$, t], δ 3.05 [$N(CH_2CH_3)_3$, q], δ 2.09 [(CH_3, Pz) , s], δ 5.72 [(CH, Pz) , s], ^{31}P NMR (500 MHz, $DMSO-d_6$): δ 3.15(s).

Instrumentation:

Melting points were measured using a JSGW melting point apparatus and are uncorrected. IR spectra were recorded as KBr pellets on a Perkin Elmer Spectrum Version FT IR spectrophotometer operating at 400-4000 cm^{-1} . Elemental analyses of the compounds were obtained from Thermoquest CE instruments CHNS-O, EA/110 model. Electrospray ionization mass spectrometry (ESI-MS) spectra were recorded on a Micromass Quattro II triple quadrupole mass spectrometer. Thermogravimetric analysis (heating rate of 10 $^{\circ}\text{C min}^{-1}$) was carried out on a Perkin-Elmer Pyris 6 machine.

X-ray Crystallography:

Data were collected on Bruker APEX II CCD diffractometer ($\text{MoK}\alpha$, $\lambda = 0.71073 \text{ \AA}$). Complete hemispheres of data were collected using ω -scans (0.3° , up to 30 s/frame). Integrated intensities were obtained with SAINT+,^{S3} and when they were corrected for absorption SADABS was used.^{S4} Structure solution and refinement was performed with the SHELXTL-package.^{S5} The structures were solved by direct methods and completed by iterative cycles of DF syntheses and full-matrix least-squares refinement against F^2 .^{S6} All the other non-hydrogen atoms were refined with anisotropic displacement parameters. All the hydrogen atoms on the carbon frameworks were included in the final stages of the refinement and were refined with a typical riding model. Some solvent molecules could not be modeled satisfactorily as they were located on the symmetry elements of the space group. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, U.K. Fax: +44-1223/336-033. E-mail: deposit@ccdc.cam.ac.uk].

References:

- (S1) S. Bengelsdorf, and L. B. Barron, *J. Am. Chem. Soc.* 1955, **77**, 2869.
- (S2) B. S. Furniss, A. J. Hannaford, P. W. G. Smith and A. R. Tatchell, *Vogel's Text book of Practical Organic Chemistry*, 5th edn, ELBS, Longman, London, 1989.
- (S3) *SMART & SAINT Software Reference Manuals, version 6.45; Bruker Analytical X-ray Systems, Inc.:* Madison, WI, 2003.
- (S4) G. M. Sheldrick, *SADABS a Software for Empirical Absorption Correction, version 2.05;* University of Göttingen: Göttingen, Germany, 2002.
- (S5) G. M. Sheldrick, *SHELXTL, version 6.12; Bruker AXS Inc.* Madison, WI, 2001.
- (S6) G. M. Sheldrick, *SHELXL97, Program for Crystal Structure Refinement*, University of Göttingen: Göttingen, Germany, 1997.

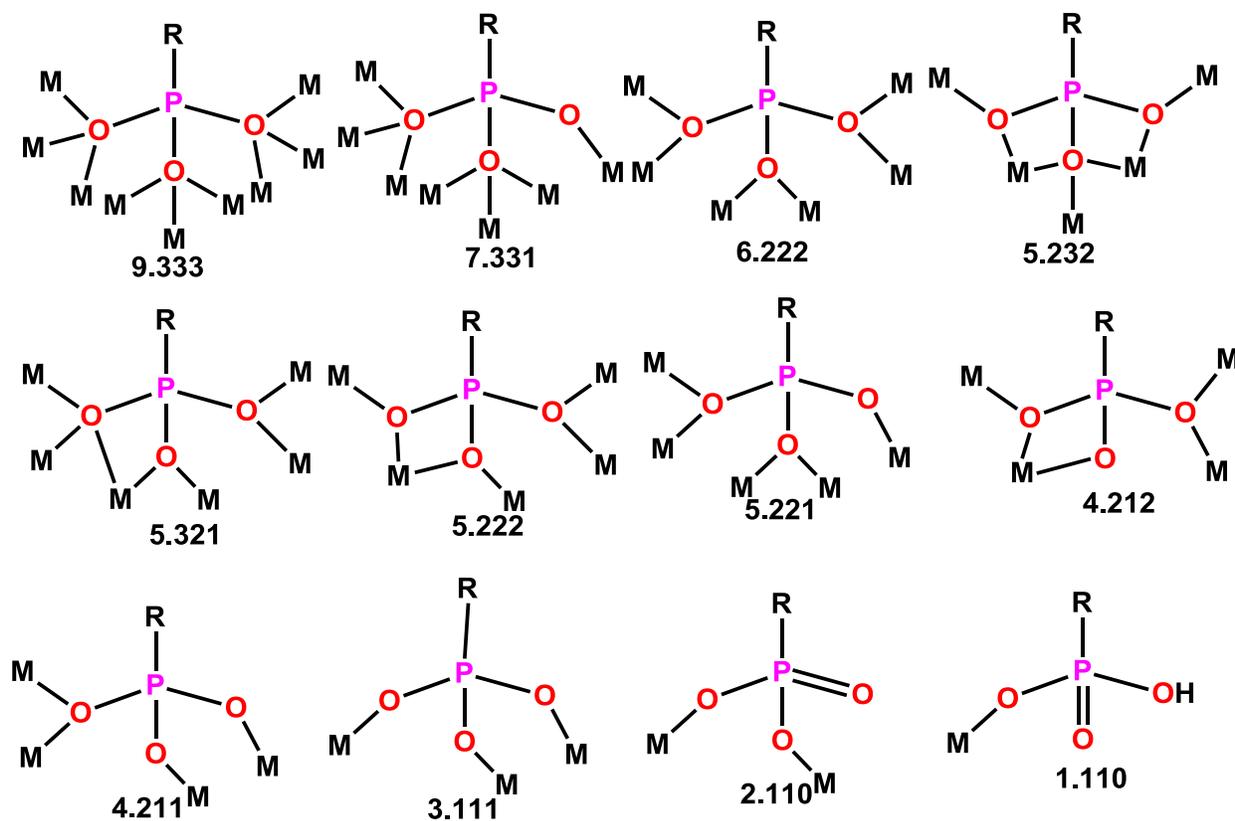


Chart S1: Binding capacity of the phosphonate ligand (Harris notation has been used).

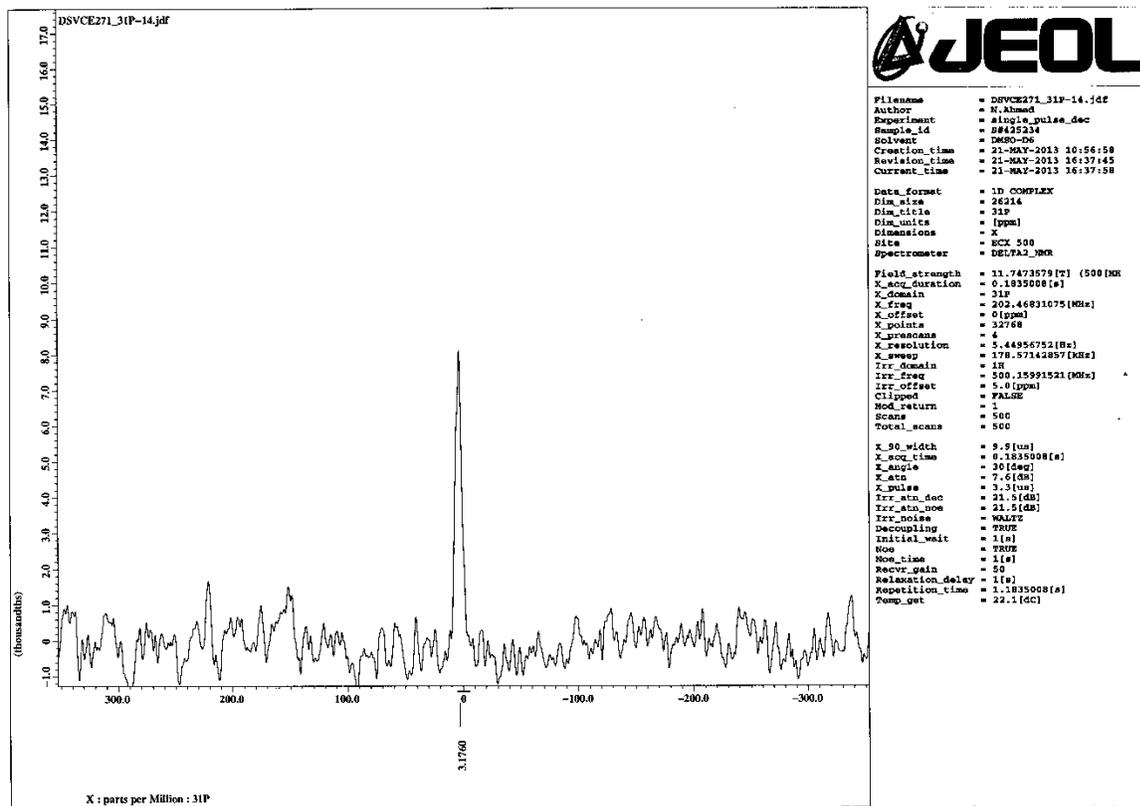


Fig. S1 ^{31}P NMR of 2.

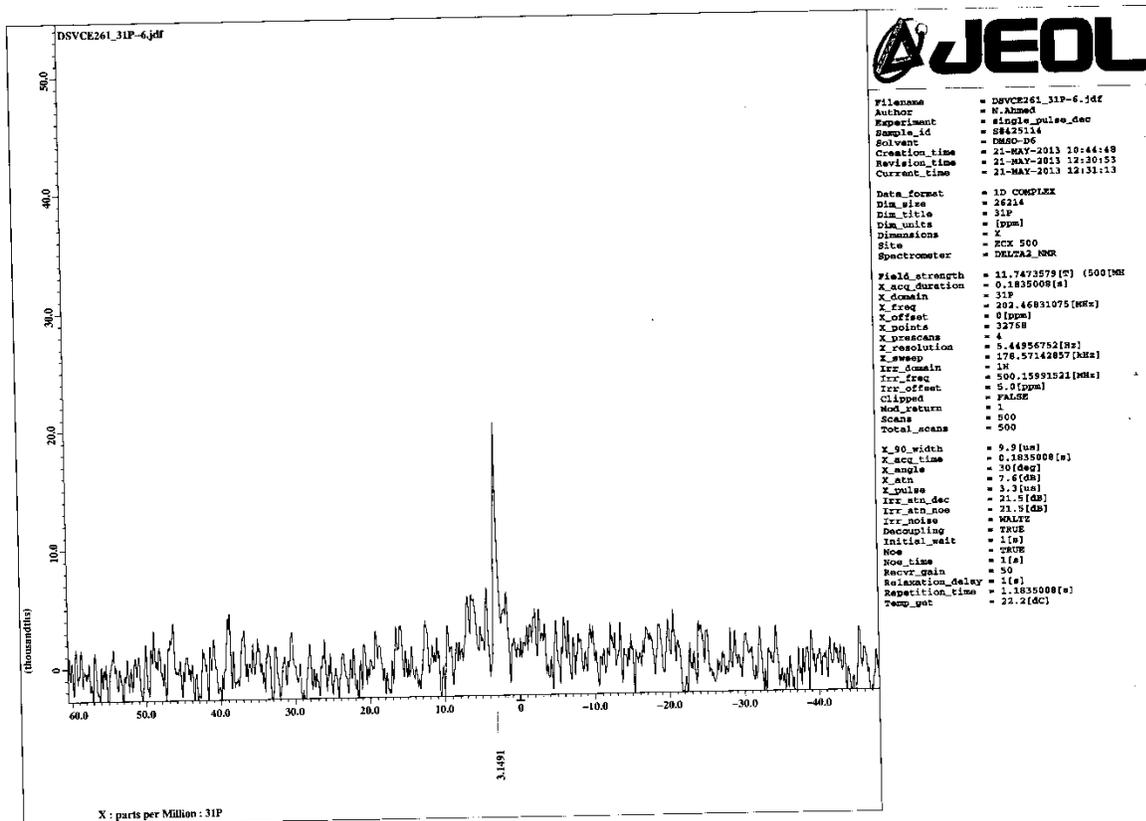


Fig. S2 ^{31}P NMR of 4.

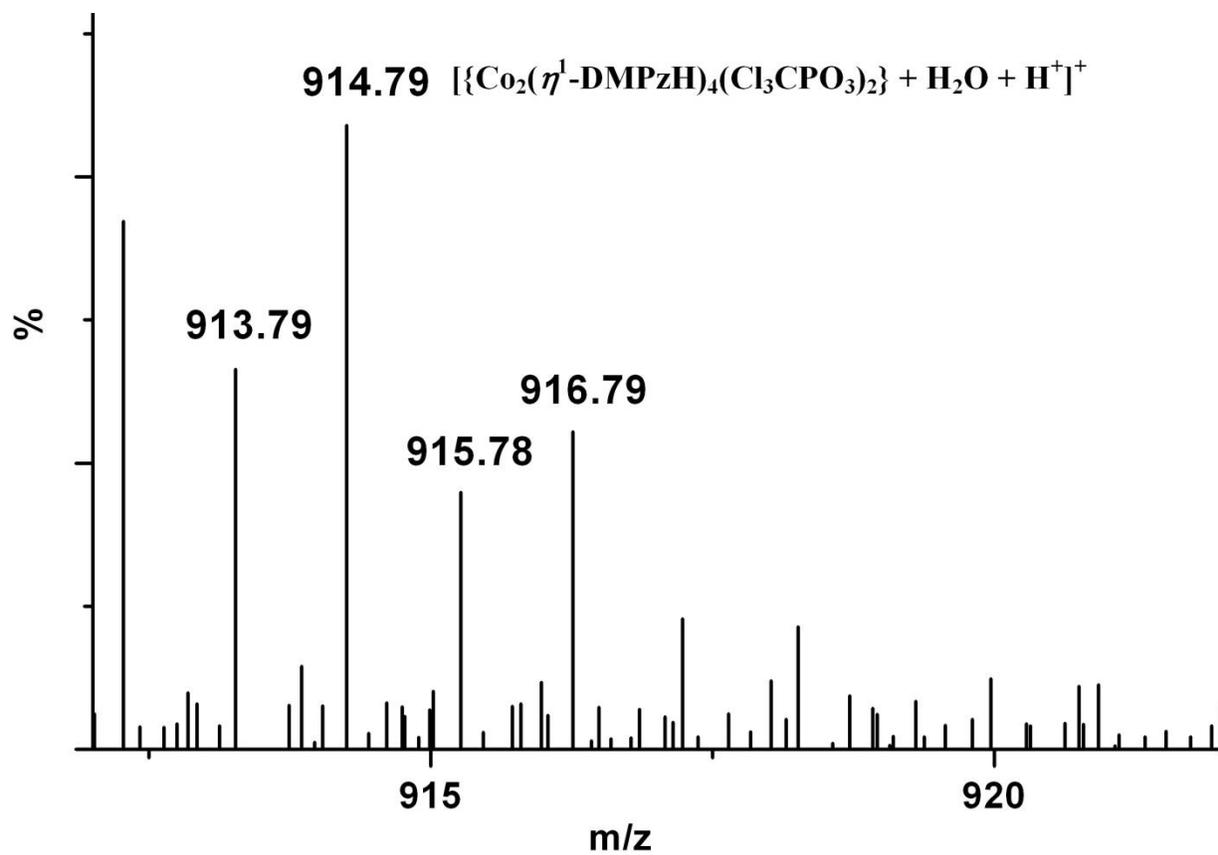


Fig. S3 ESI-MS of 1.

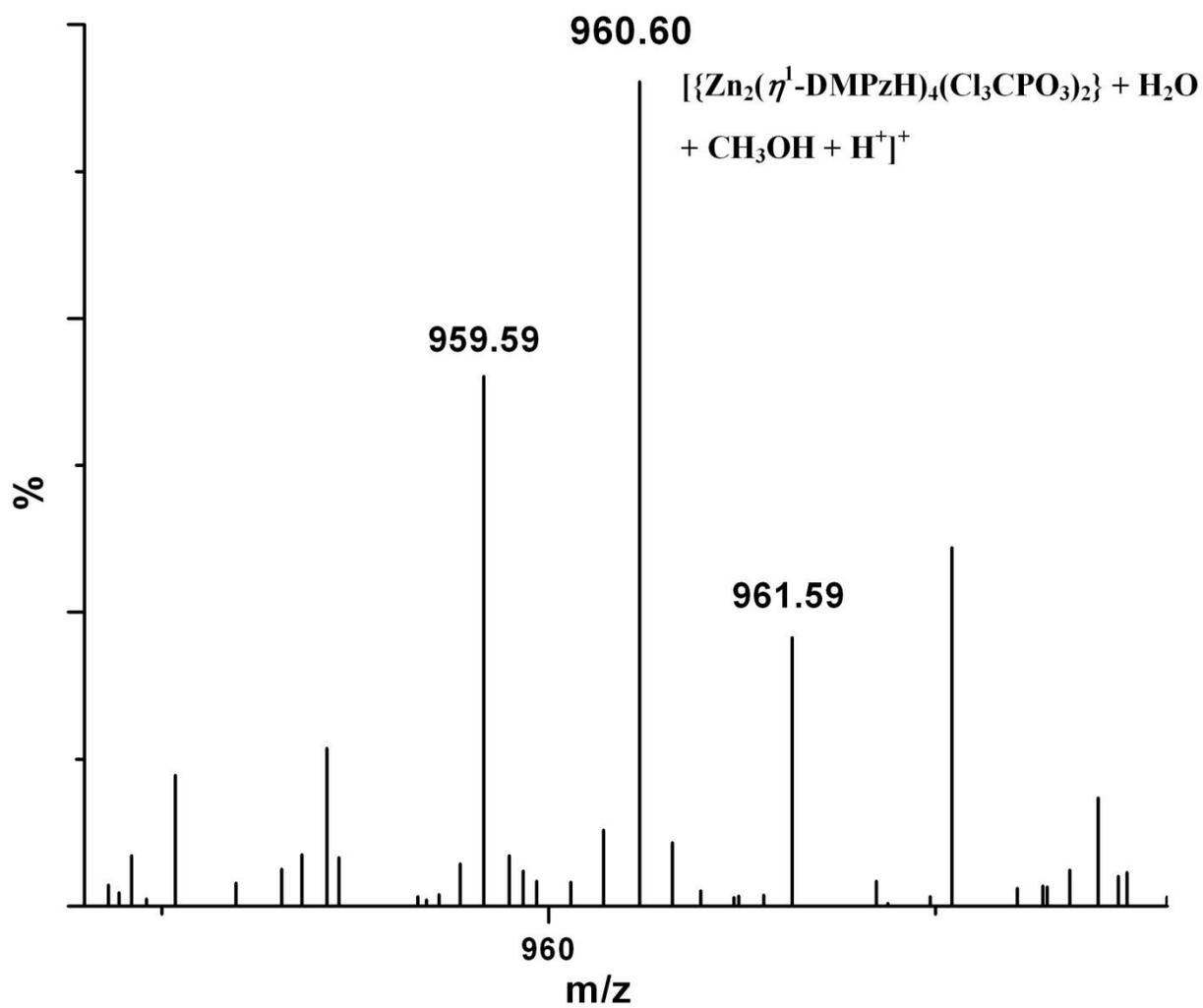


Fig. S4 ESI-MS of 2.

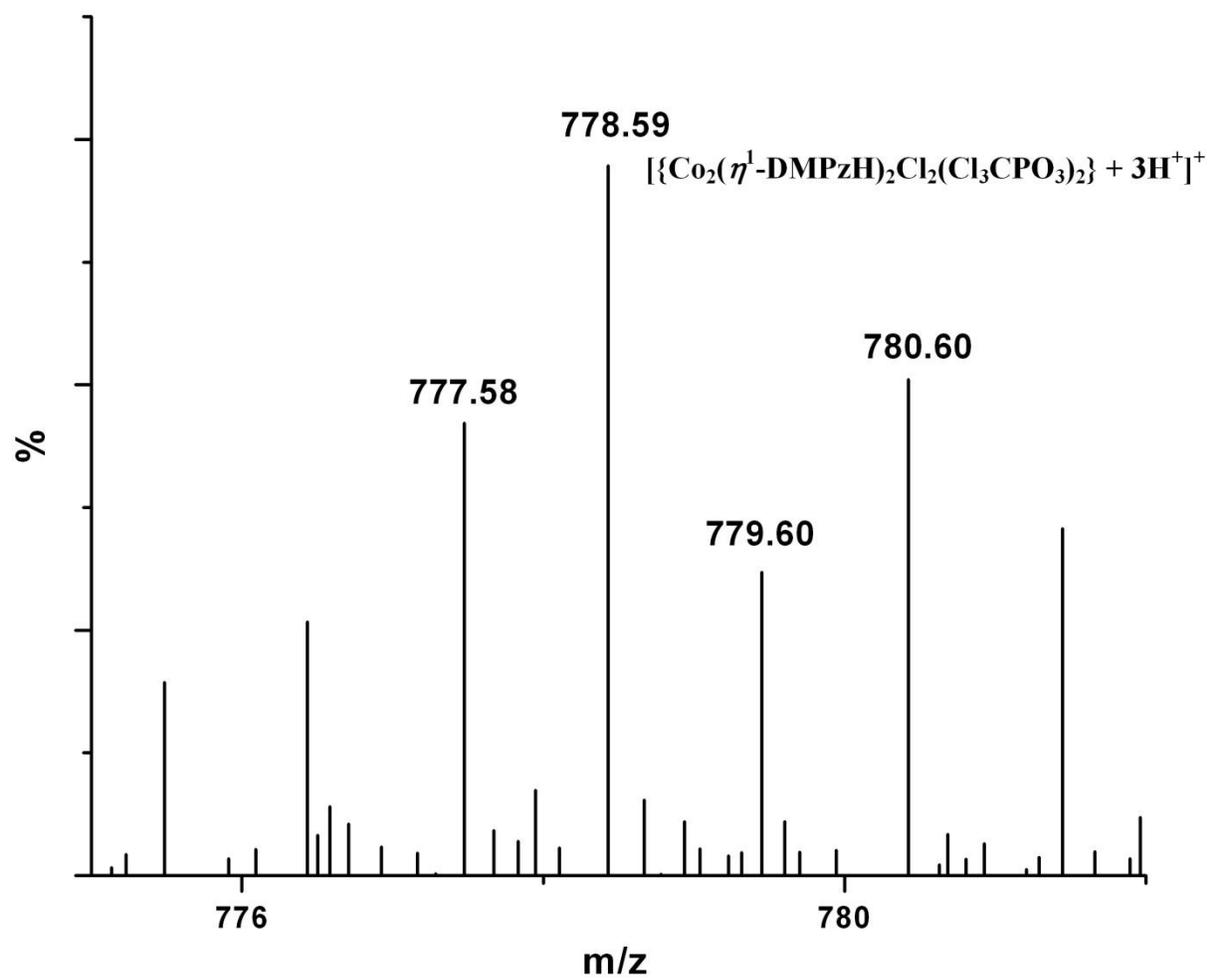


Fig. S5 ESI-MS of **3**.

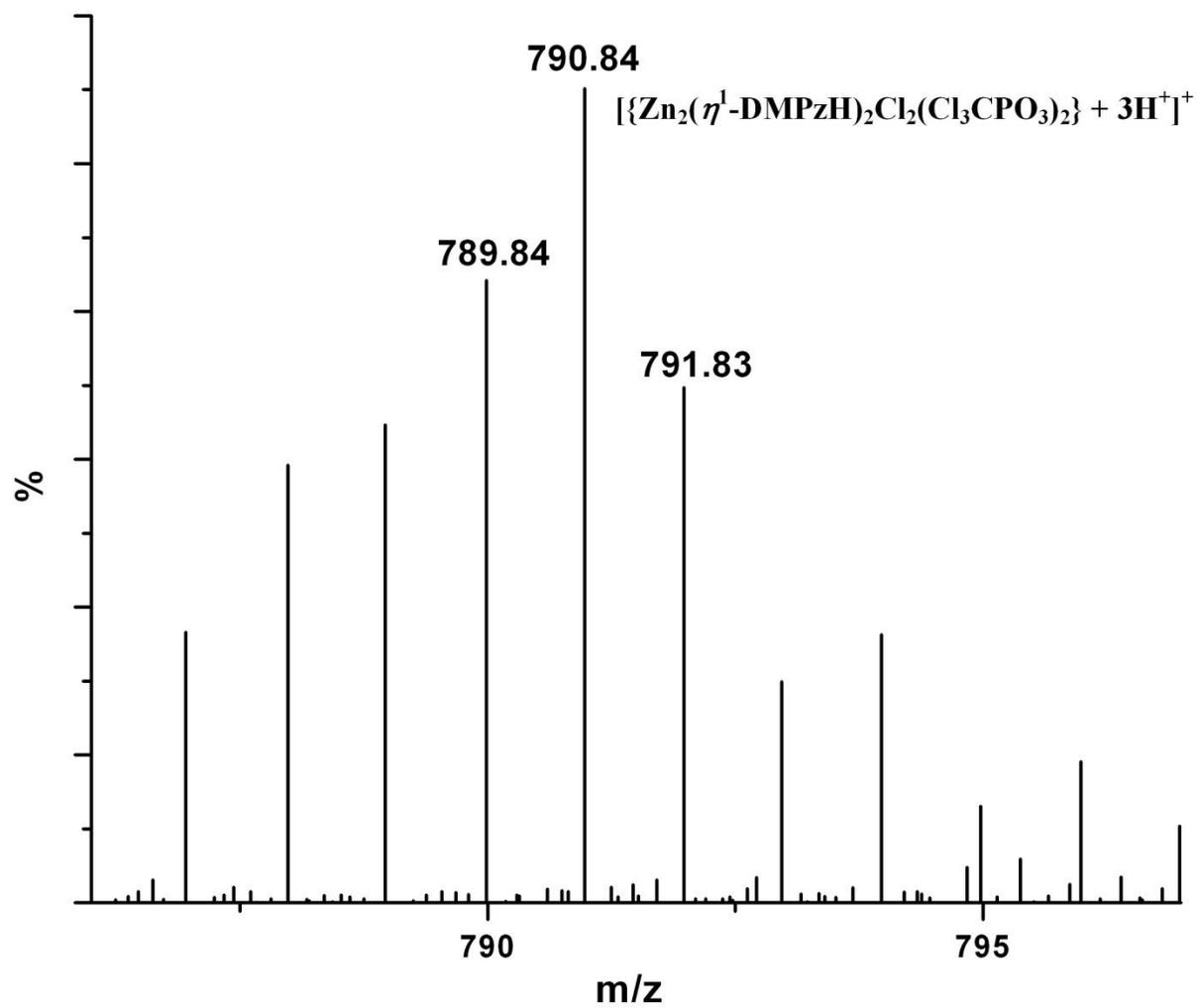


Fig. S6 ESI-MS of 4.

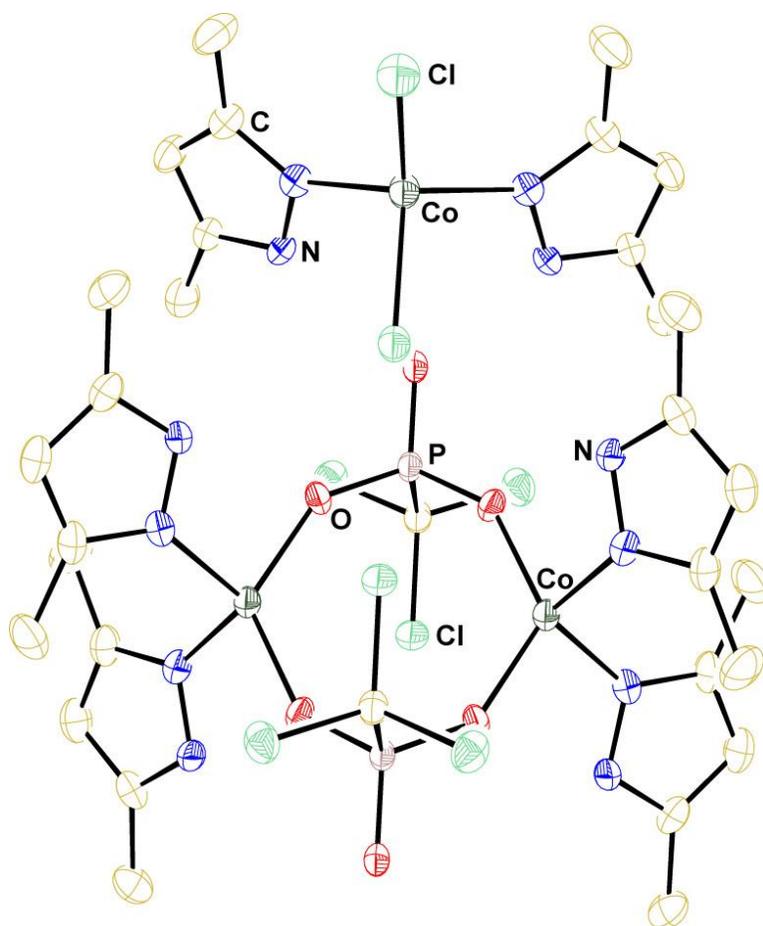


Fig. S7 ORTEP diagram of **1** with 50% thermal ellipsoids. All H atoms and toluene molecules have been deleted for clarity.

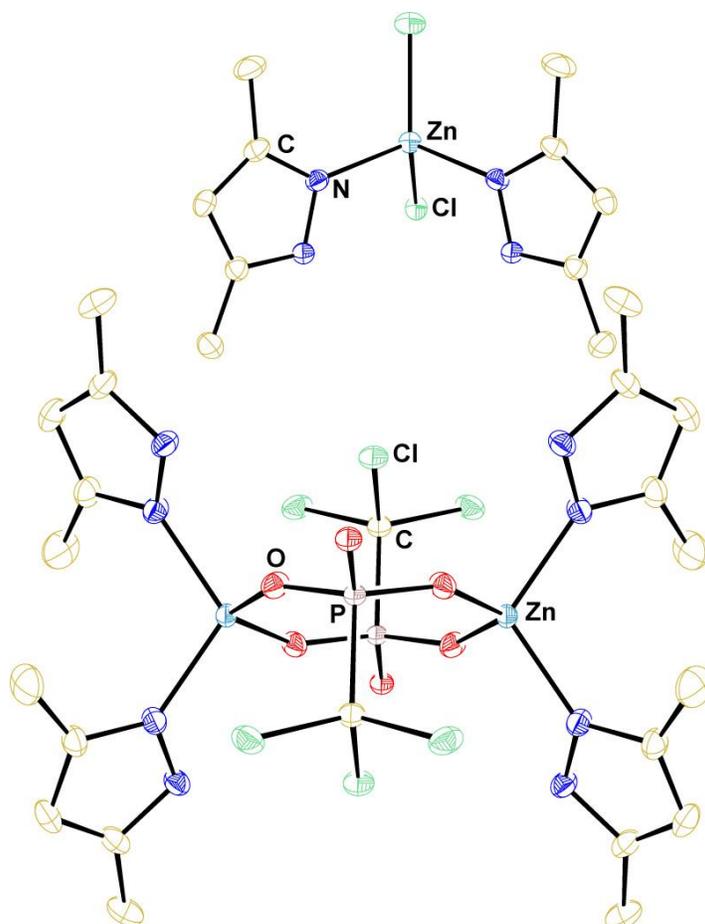


Fig. S8 ORTEP diagram of **2** with 50% thermal ellipsoids. All H atoms and toluene molecules have been deleted for clarity.

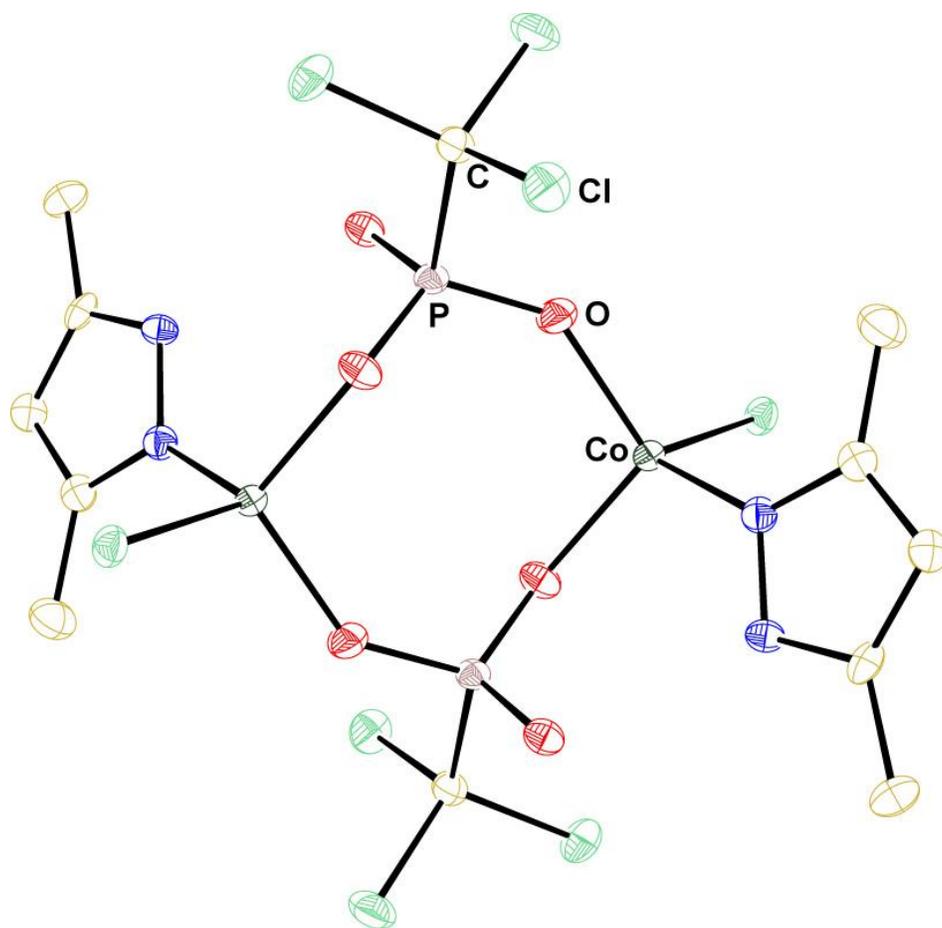


Fig. S9 ORTEP diagram of **3** with 50% thermal ellipsoids. All H atoms and counter cations (Et_3NH^+) have been deleted for clarity.

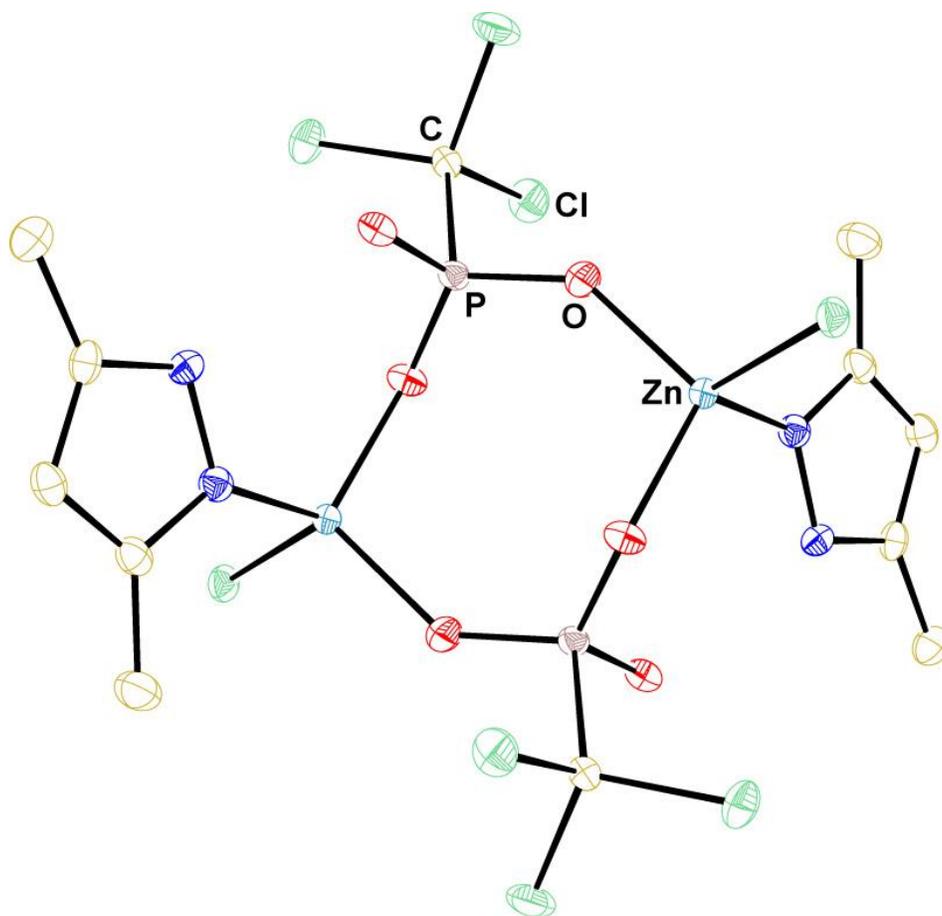


Fig. S10 ORTEP diagram of **4** with 50 % thermal ellipsoids. All H atoms and counter cations (Et_3NH^+) have been deleted for clarity.

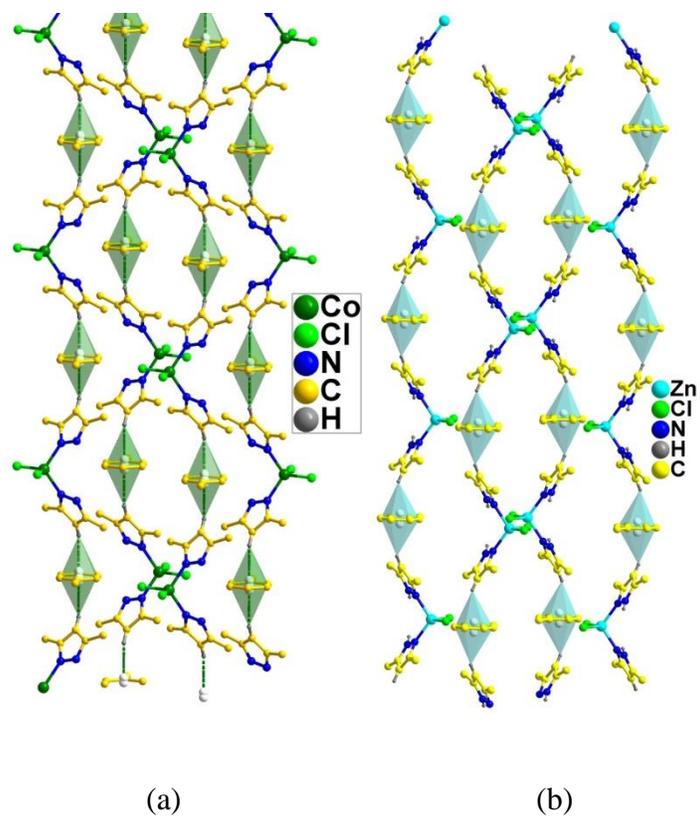


Fig. S11 (a) C-H- π interactions ($C(sp^2)$ -H of 3,5-dimethylpyrazole and toluene) in **1**. (b) C- H- π interaction ($C(sp^2)$ -H of 3,5-dimethylpyrazole and toluene) in **2**.

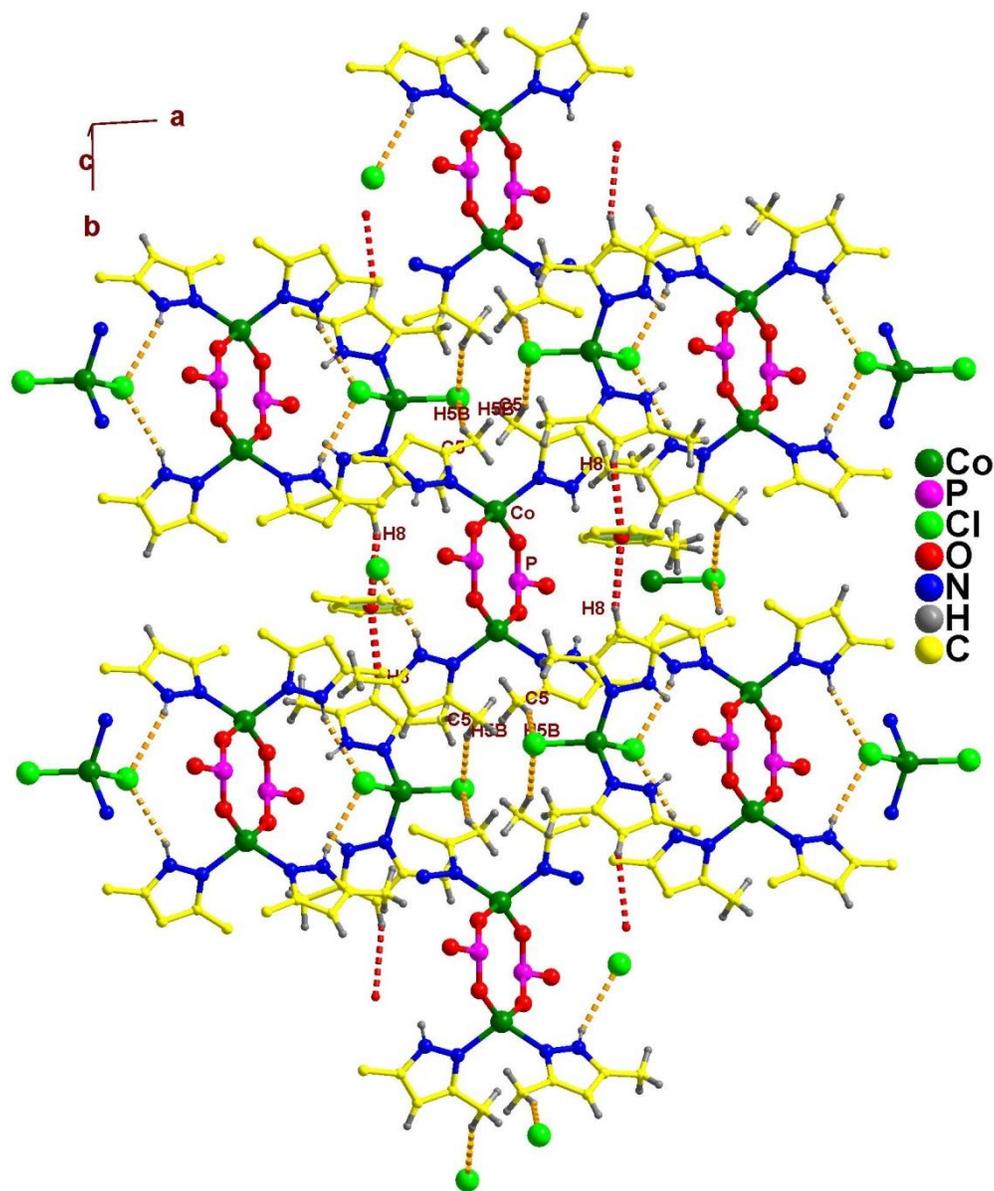


Fig. S12 2D view of the supramolecular of **1**. CCl_3 groups and some hydrogen atoms have been deleted for clarity.

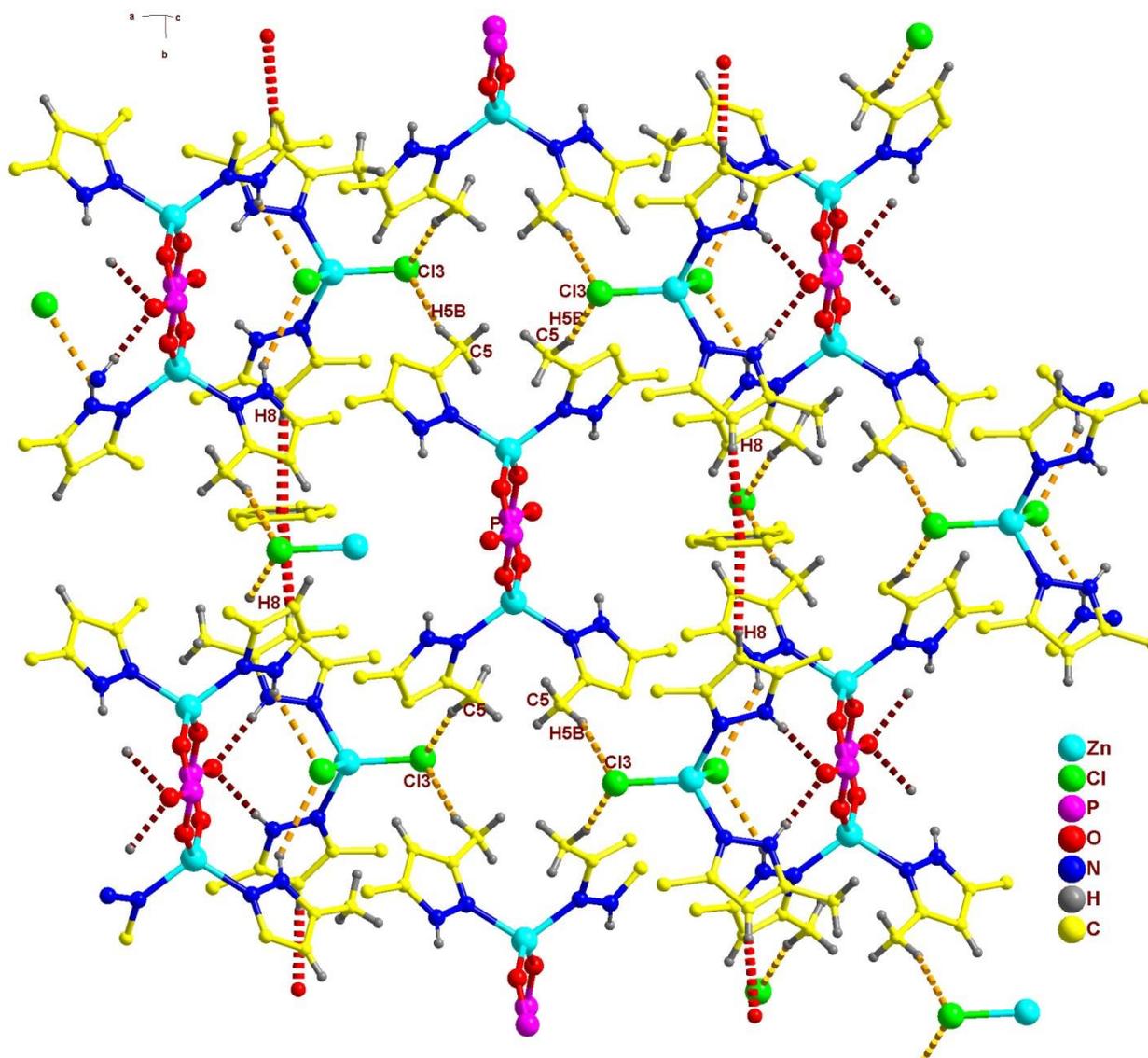


Fig. S13 2D view of the supramolecular structure of **2** (Table S4). CCl_3 groups and some hydrogen atoms have been deleted for clarity.

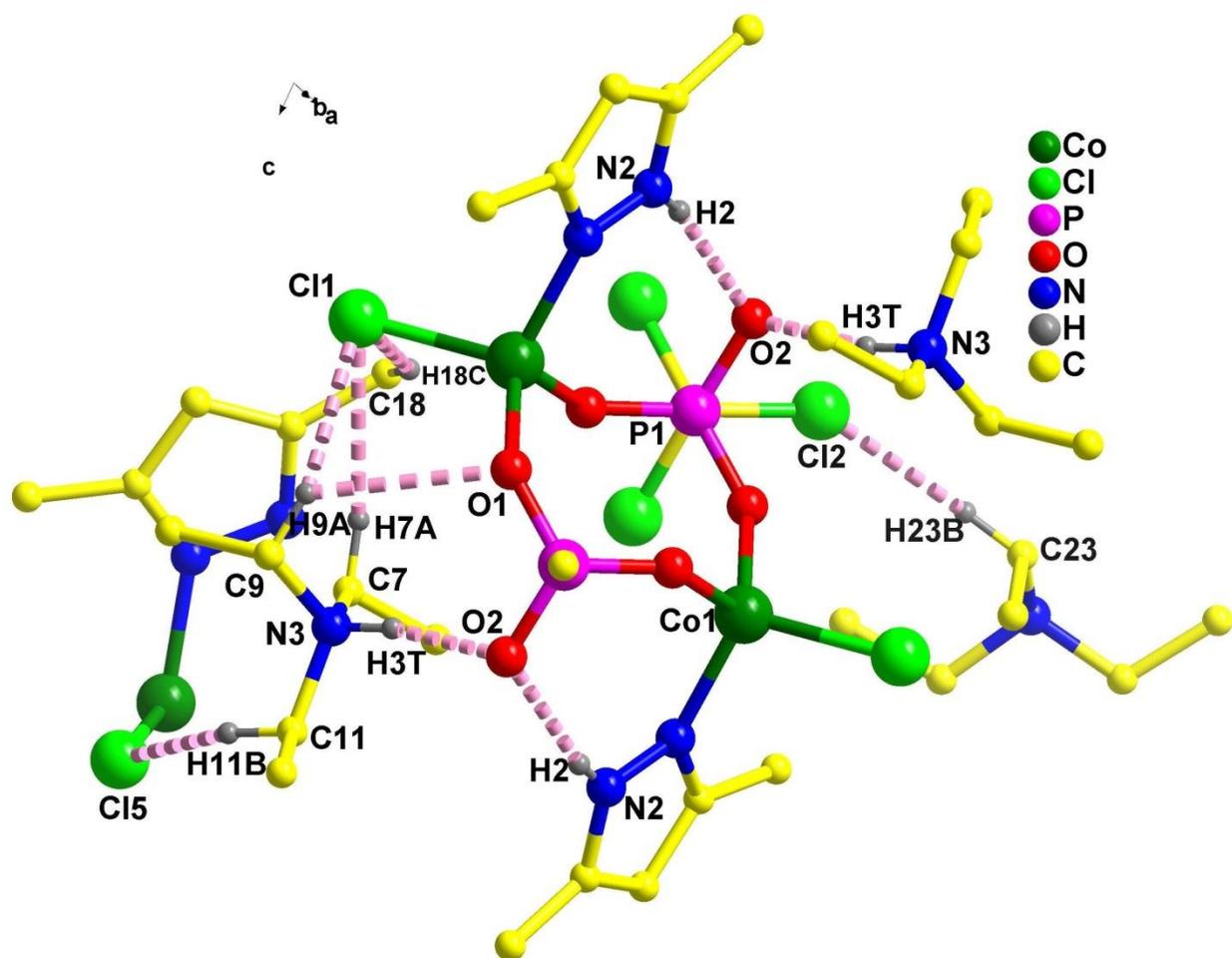


Fig. S14 Some hydrogen bonding interactions in **3** (Table S5). Some hydrogen atoms have been deleted for clarity

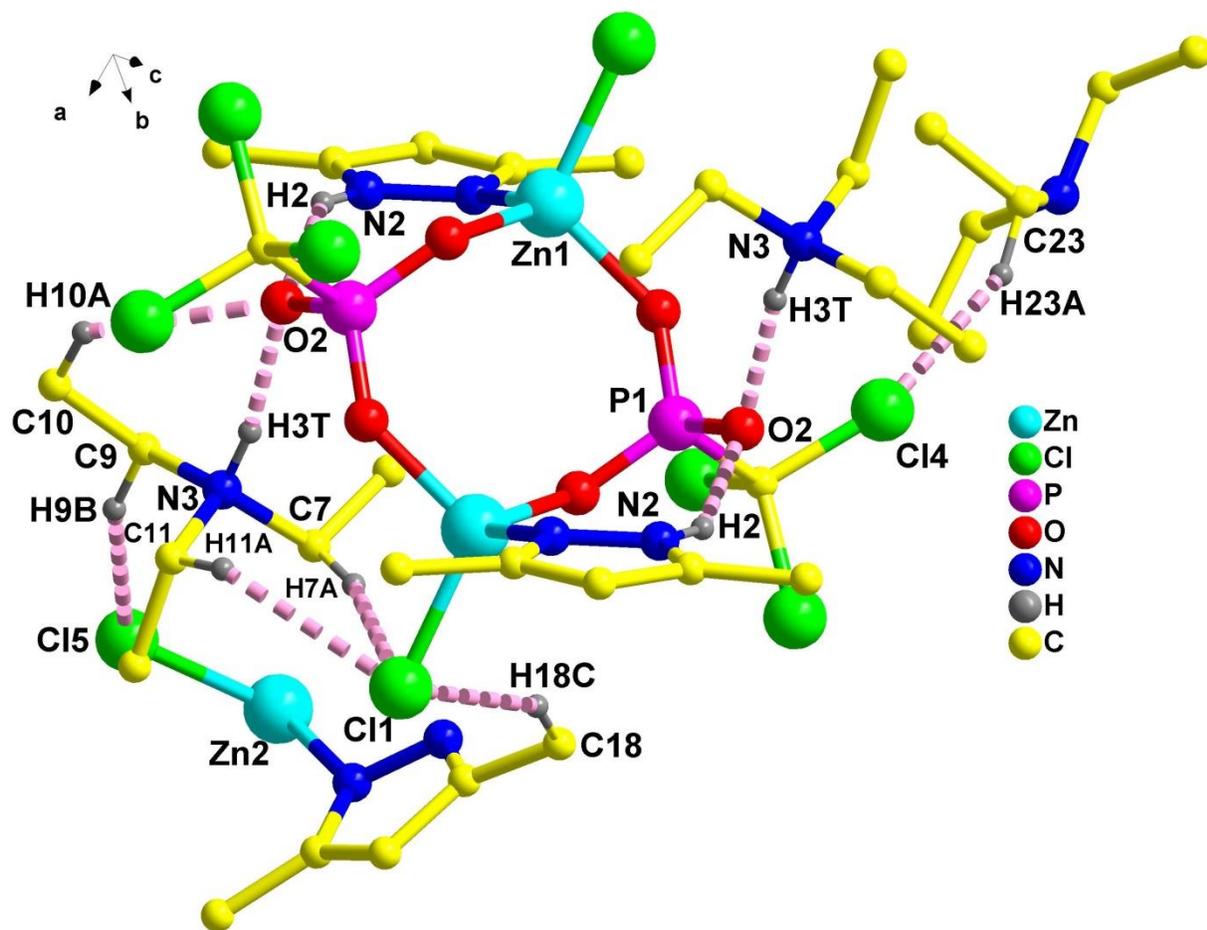


Fig. S15 Some hydrogen bond interactions in 4. Some hydrogen atoms have been deleted for clarity

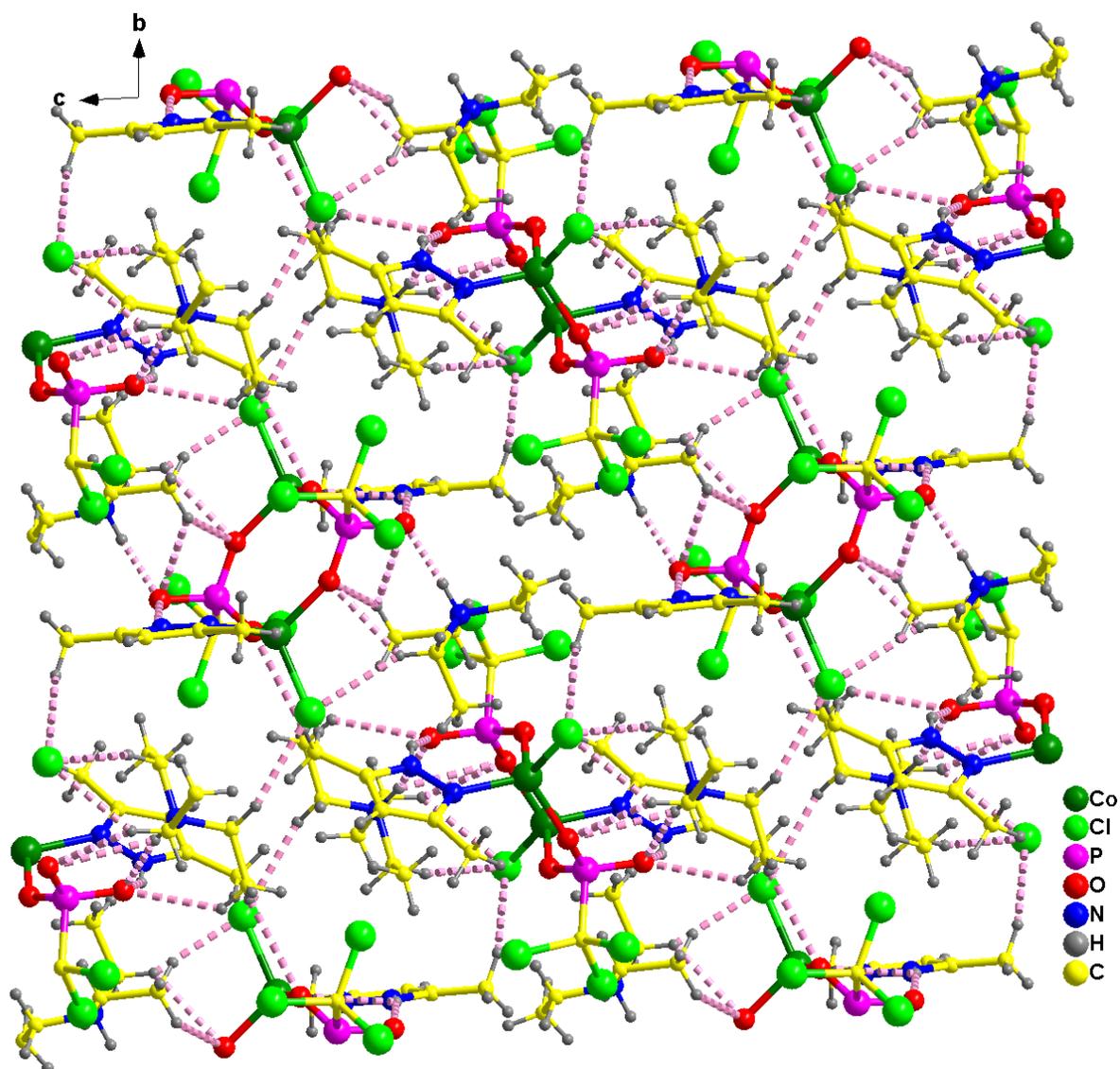


Fig. S16 3D view of the supramolecular structure of 3.

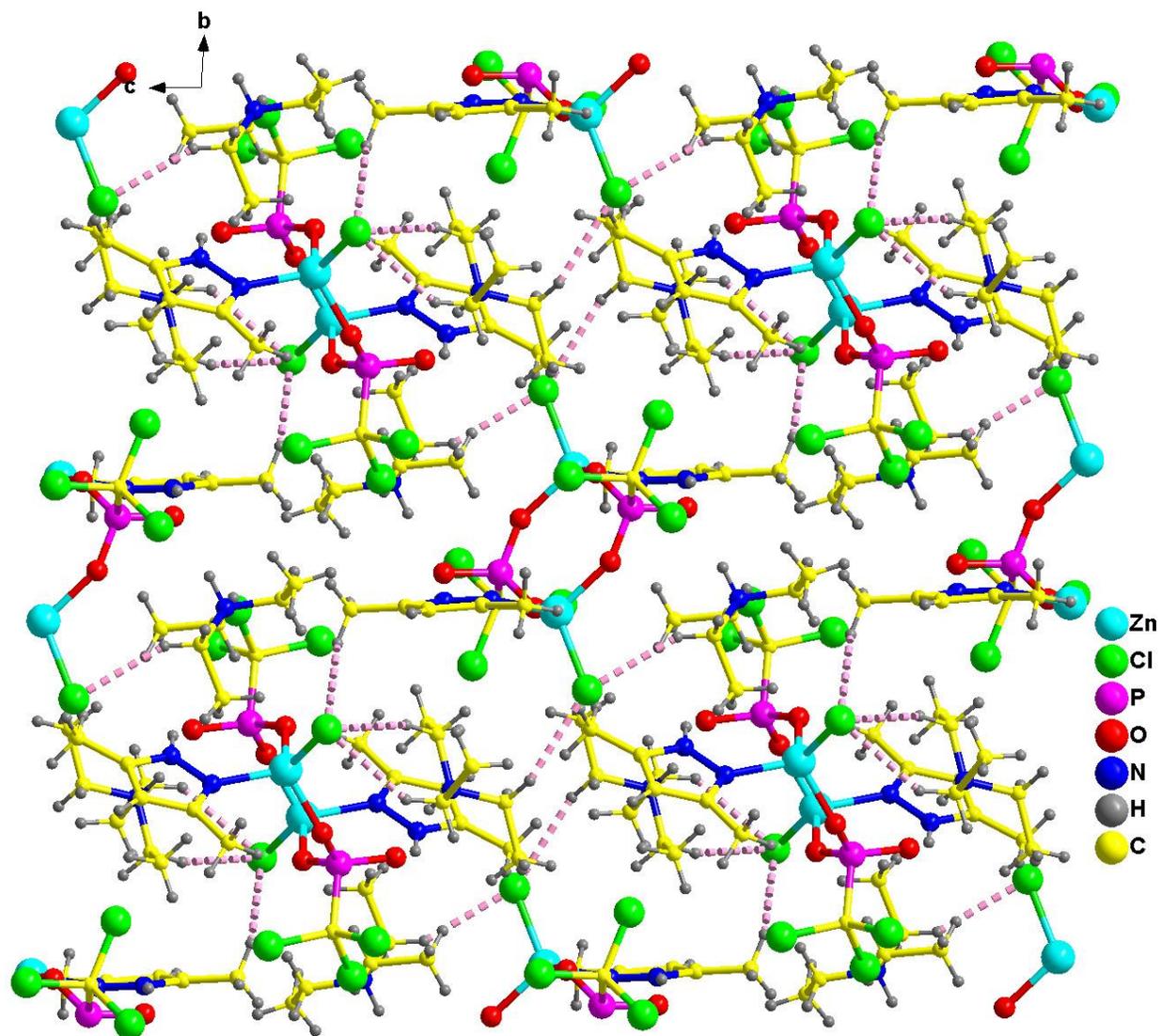


Fig. S17 3D view of the supramolecular structure of **4**.

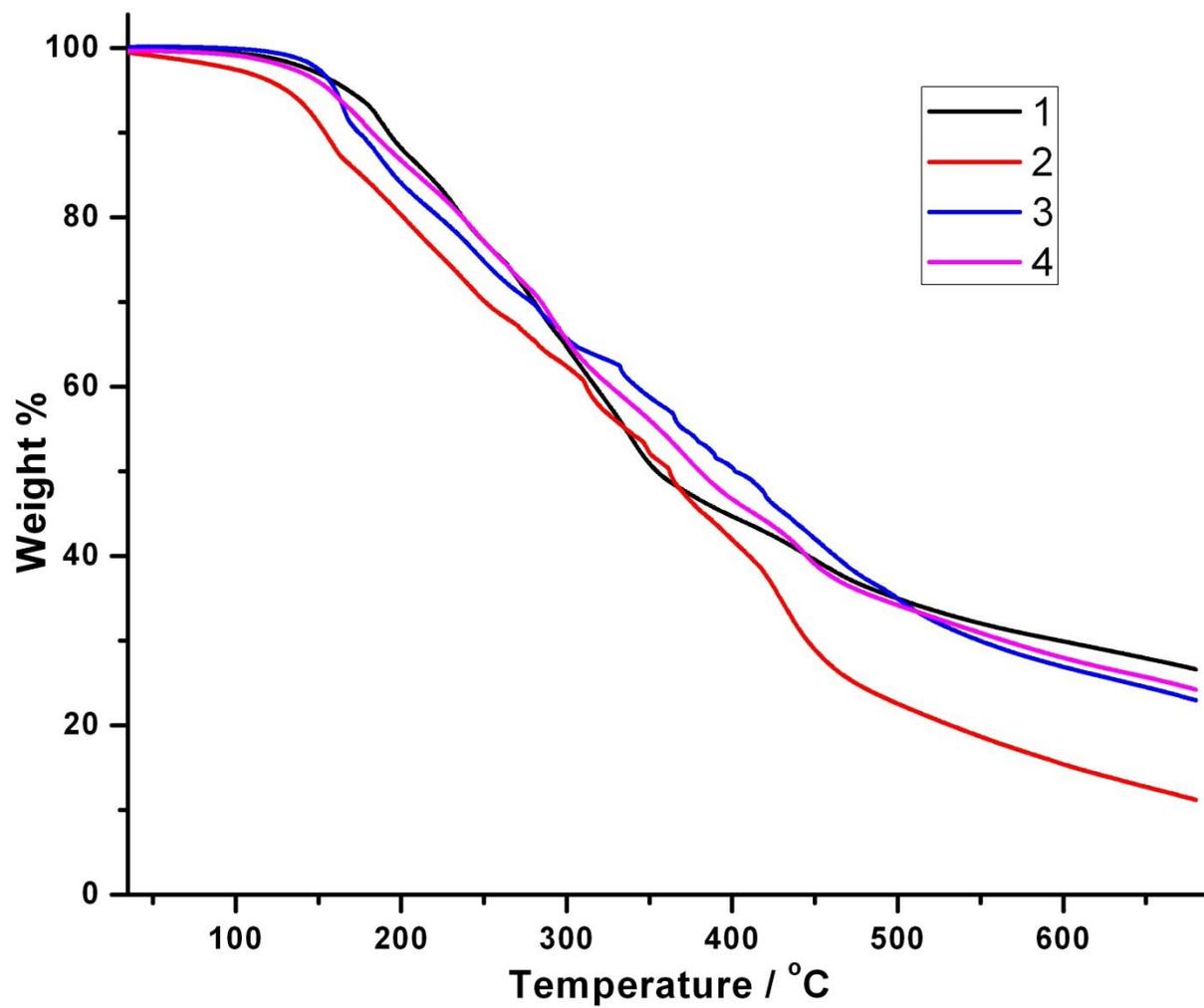


Fig. S18 TGA plots of 1-4.

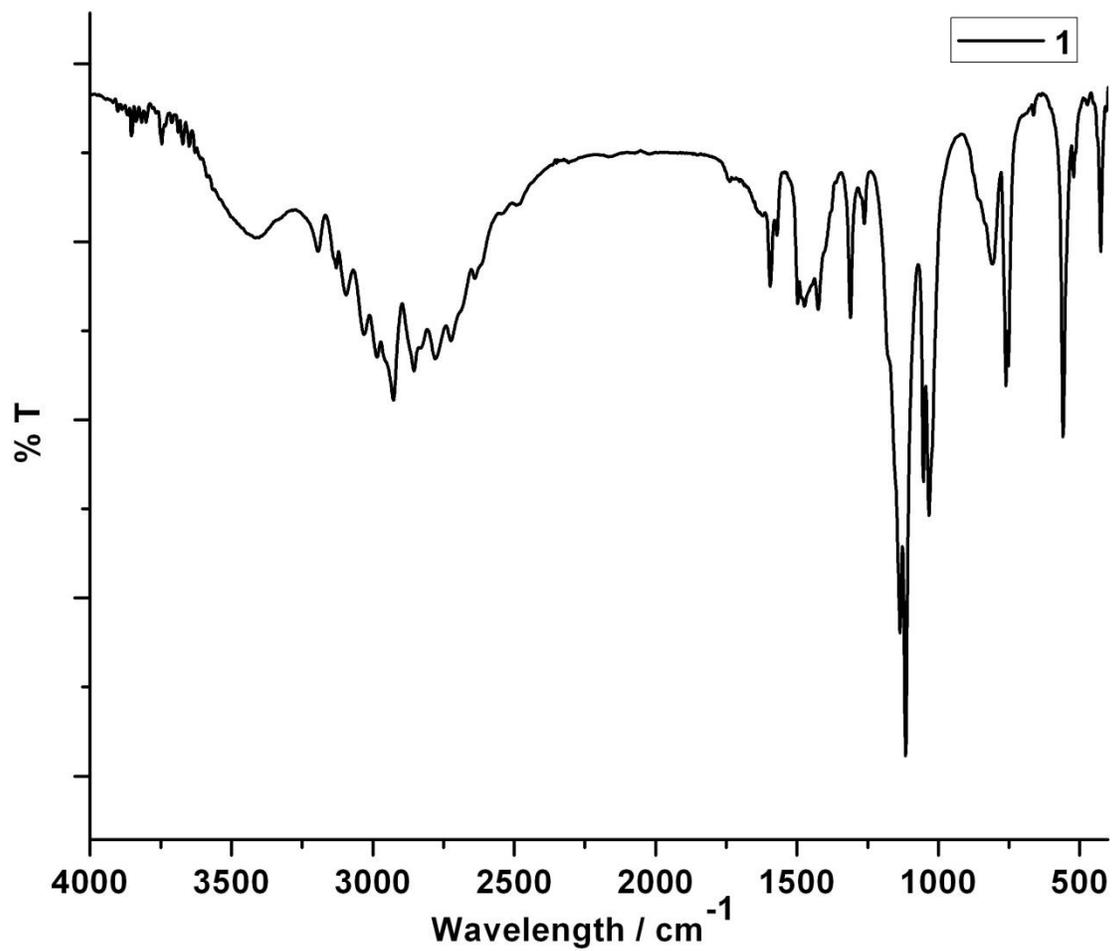


Fig. S19 IR spectrum of **1**.

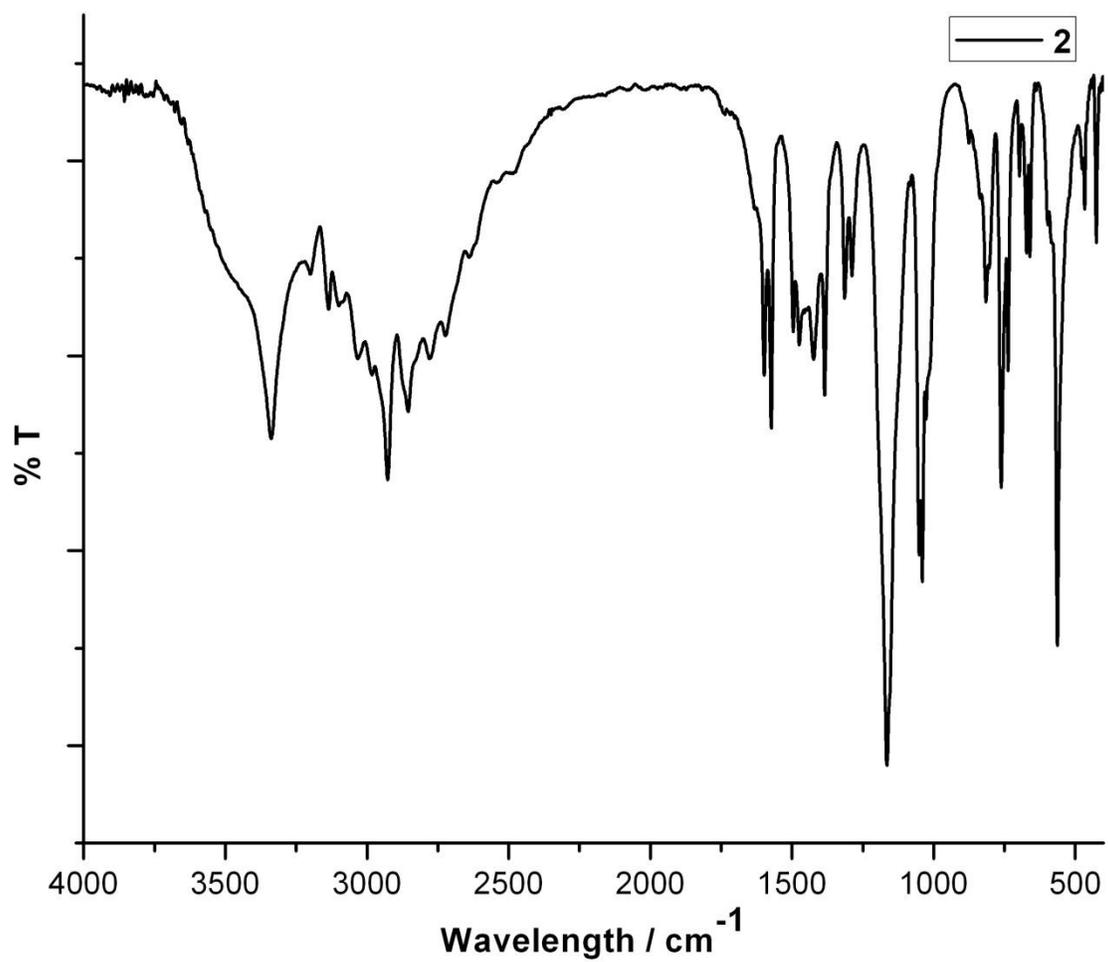


Fig. S20 IR spectrum of **2**.

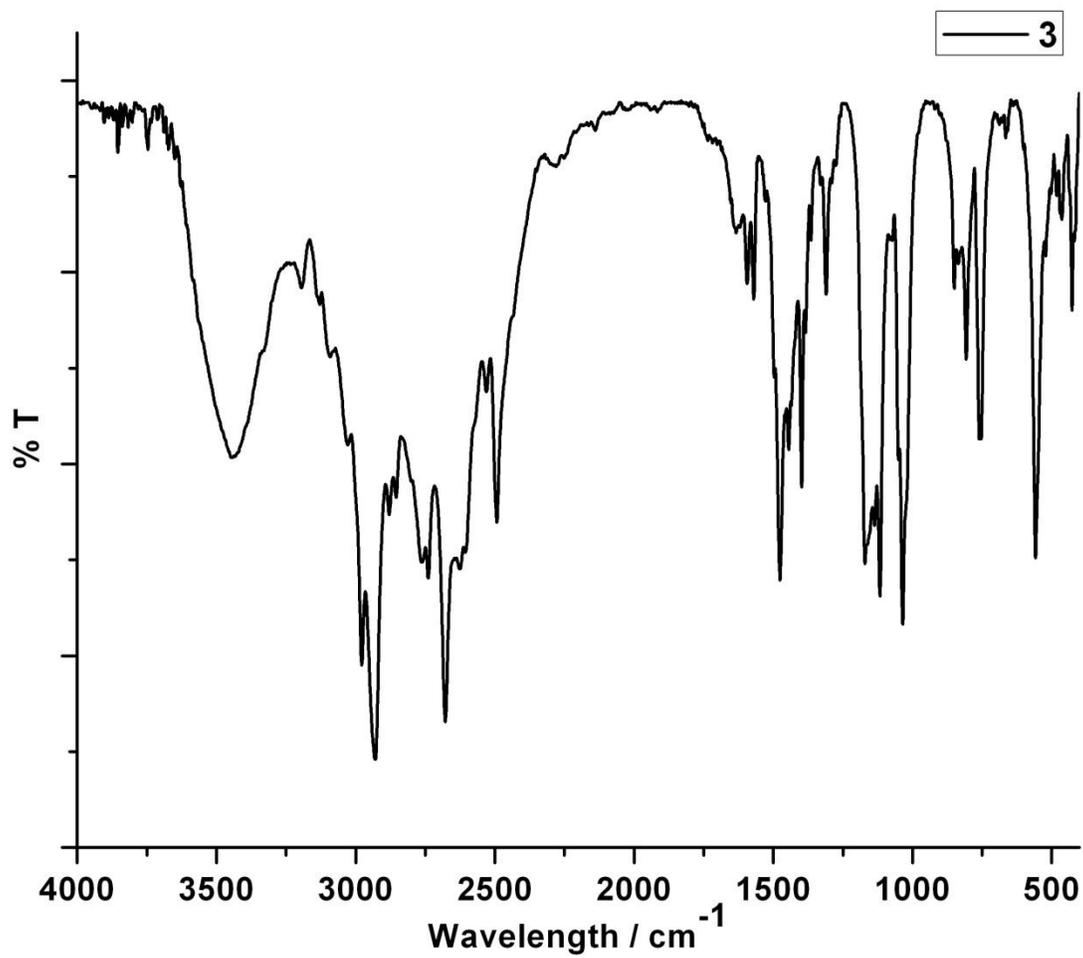


Fig. S21 IR spectrum of **3**.

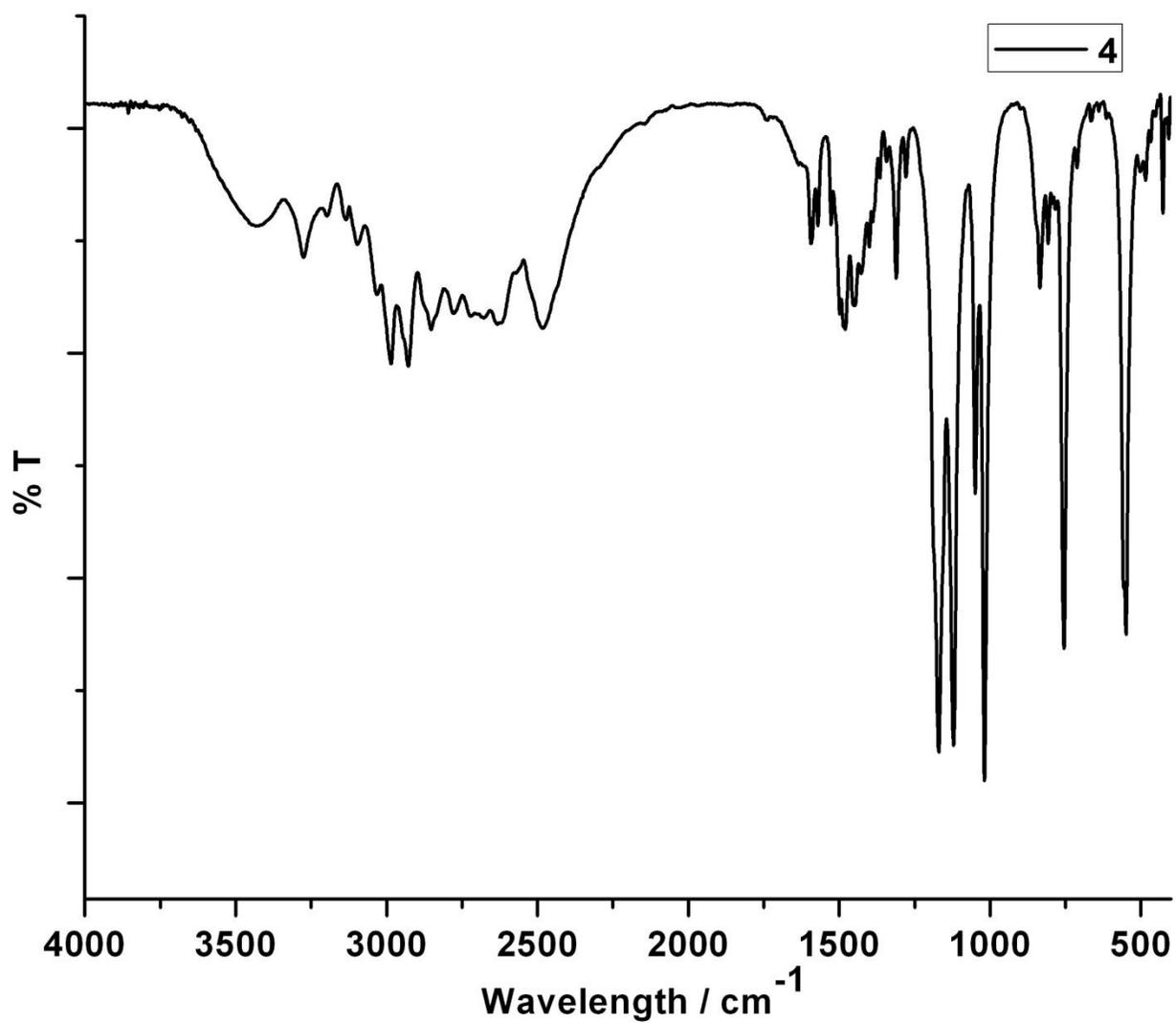


Fig. S22 IR spectrum of 4.

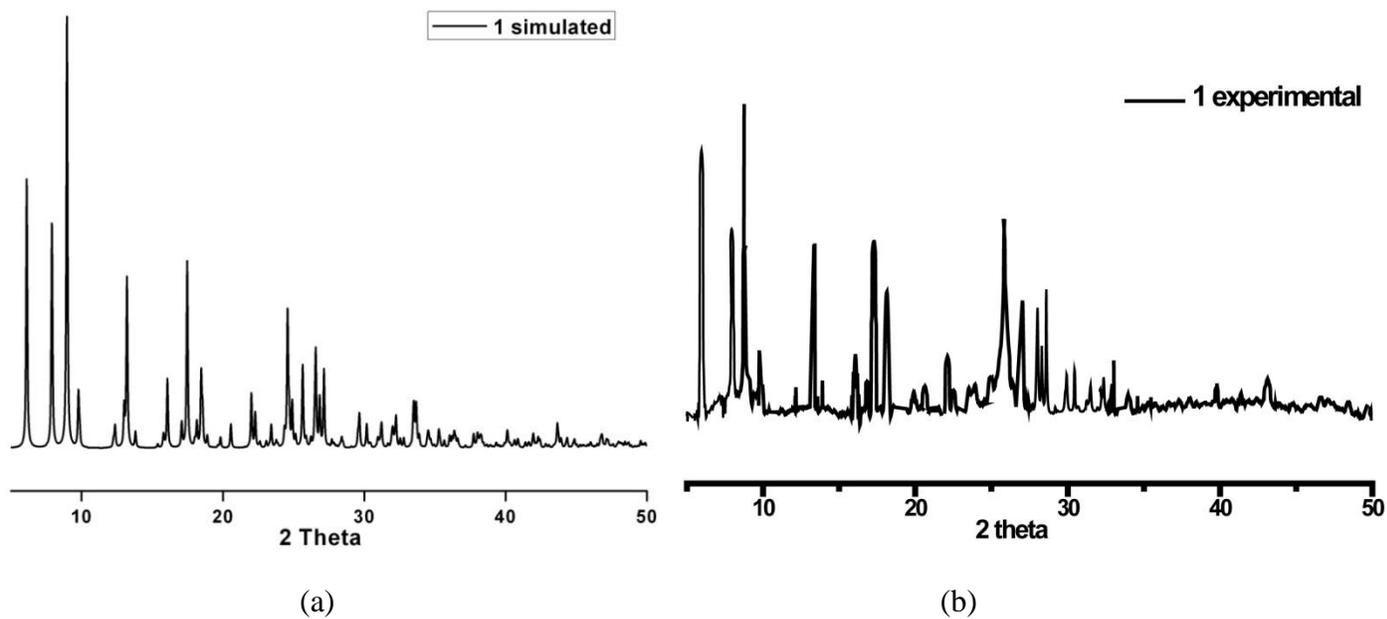


Figure S23. (a) PXRD from single crystal diffraction data (b) PXRD of the bulk sample of **1**.

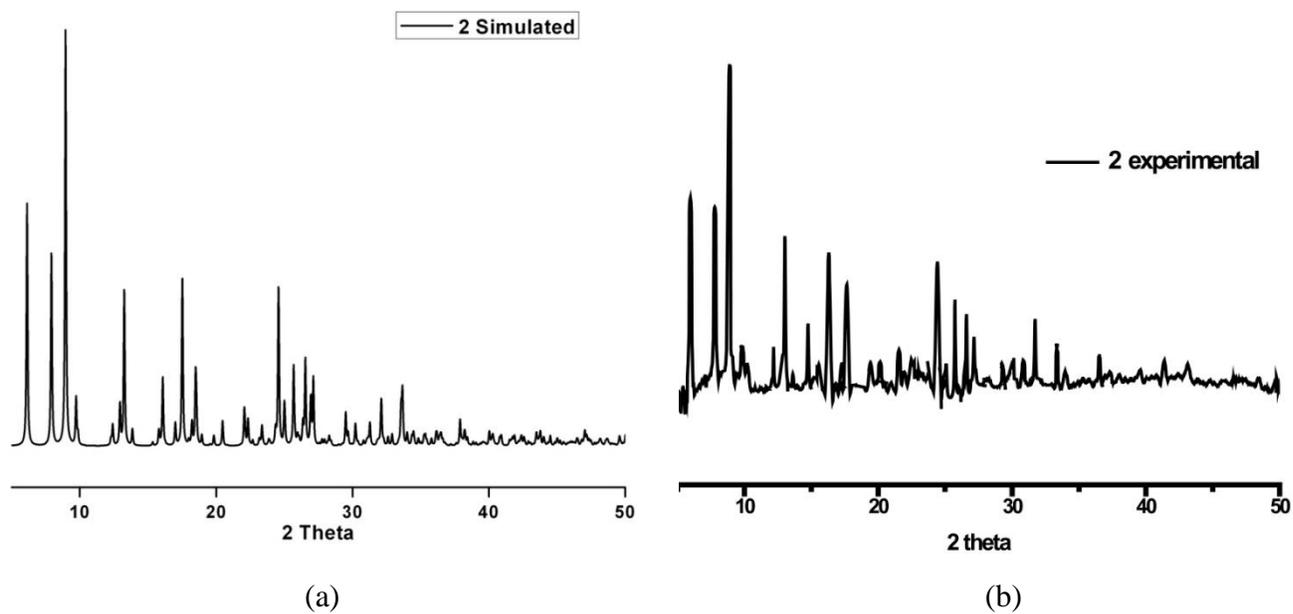


Figure S24. (a) PXRD from single crystal diffraction data (b) PXRD of the bulk sample of **2**.

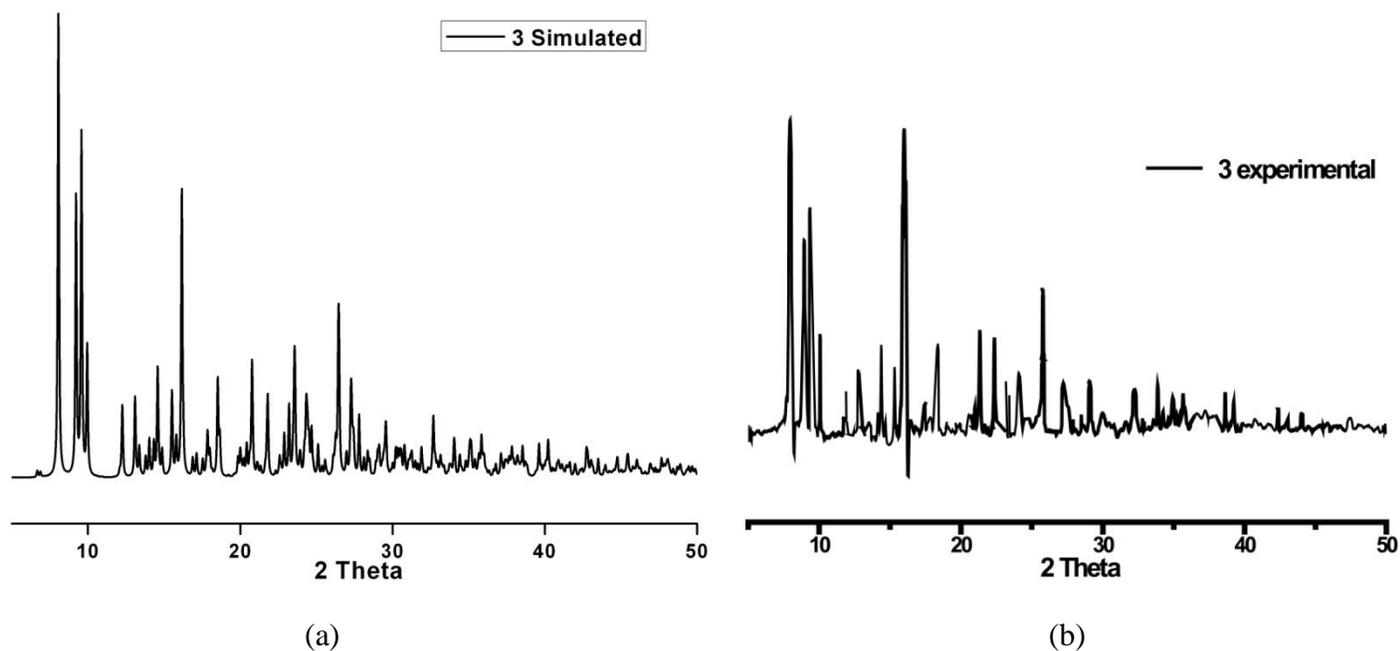


Figure S25. (a) PXRD from single crystal diffraction data (b) PXRD of the bulk sample of **3**.

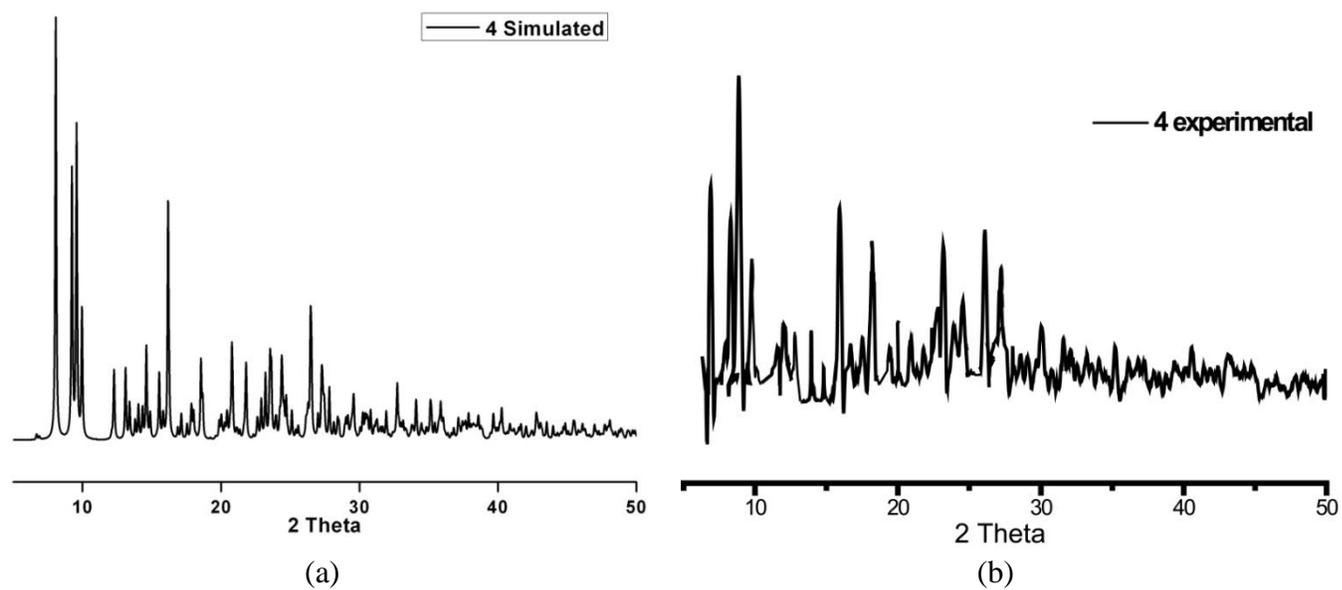


Figure S26. (a) PXRD from single crystal diffraction data (b) PXRD of the bulk sample of **4**.

Table S1. Details of the data collection and refinement parameters for **1-4**.

Crystallographic information files (CIFs) for **1-4**. **CCDC 942397-942400**.

	1	2	3	4
Empirical formula	C ₅₆ H ₈₀ Cl ₁₀ N ₁₆ O ₆ P ₂ Co ₄	C ₅₆ H ₈₀ Cl ₁₀ N ₁₆ O ₆ P ₂ Zn ₄	C ₂₄ H ₄₈ Cl ₈ N ₆ O ₆ P ₂ Co ₂	C ₂₄ H ₄₈ Cl ₈ N ₆ O ₆ P ₂ Zn ₂
Formula weight	1725.52	1751.36	980.08	993.00
Temperature	100(2) K	100(2) K	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic	triclinic	triclinic
Space group	C 2/m	C 2/m	P-1	P-1
Unit cell dimensions	$a = 18.985(5)$ Å $\alpha = 90^\circ$	$a = 18.985(5)$ Å $\alpha = 90^\circ$	$a = 12.271(5)$ Å $\alpha = 87.852(5)^\circ$	$a = 12.267(5)$ Å $\alpha = 87.780(5)^\circ$
	$b = 14.293(5)$ Å $\beta = 108.950(5)^\circ$	$b = 14.238(5)$ Å $\beta = 109.480(5)^\circ$	$b = 13.575(5)$ Å $\beta = 70.724(5)^\circ$	$b = 13.569(5)$ Å $\beta = 70.635(5)^\circ$
	$c = 15.240(5)$ Å $\gamma = 90^\circ$	$c = 15.264(5)$ Å $\gamma = 90^\circ$	$c = 14.049(5)$ Å $\gamma = 71.366(5)^\circ$	$c = 14.029(5)$ Å $\gamma = 71.328(5)^\circ$
Volume	3900(2) Å ³	3890(2) Å ³	2087.2(14) Å ³	2081.1(14) Å ³
Z	2	2	2	2
Density (calculated)	1.469 Mg/m ³	1.495 Mg/m ³	1.559 Mg/m ³	1.585 Mg/m ³
Absorption coefficient	1.274 mm ⁻¹	1.658 mm ⁻¹	1.426 mm ⁻¹	1.786 mm ⁻¹
F(000)	1768	1792	1004	1016
Crystal size	0.084 × 0.082 × 0.080 mm	0.084 × 0.080 × 0.078 mm	0.084 × 0.080 × 0.078	0.084 × 0.082 × 0.078
Theta range for data collection	4.11 to 25.02 deg.	2.07 to 25.50 deg.	4.08 to 25.03deg.	4.09 to 25.03deg
Index ranges	-15 ≤ h ≤ 22, -17 ≤ k ≤ 17, -18 ≤ l ≤ 18	-16 ≤ h ≤ 22, -17 ≤ k ≤ 16, -18 ≤ l ≤ 15	-14 ≤ h ≤ 14, -15 ≤ k ≤ 16, -16 ≤ l ≤ 12	-14 ≤ h ≤ 13, -16 ≤ k ≤ 12, -16 ≤ l ≤ 16
Reflections collected	10123	13599	13503	14145
Independent reflections	3590 [$R(int) = 0.0608$]	3789 [$R(int) = 0.0265$]	7375 [$R(int) = 0.0291$]	7279 [$R(int) = 0.0202$]
Completeness to theta = 25.27°	99.2 %	99.9 %	100 %	99 %
Absorption correction	Empirical	Empirical	Empirical	Empirical
Max. and min. transmission	0.899 and 0.901	0.870 and 0.879	0.887 and 0.895	0.861 and 0.870
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	3563 / 0 / 239	3785 / 0 / 239	7375/0/449	7279/0/449
Goodness-of-fit on F^2	1.021	1.092	1.068	1.058

Final R indices [I>2σ(I)]	$R_1 = 0.0487$, $wR_2 = 0.1174$	$R_1 = 0.0248$, $wR_2 = 0.0622$	$R_1 = 0.0421$, $wR_2 = 0.0965$	$R_1 = 0.0262$, $wR_2 = 0.0620$
R indices (all data)	$R_1 = 0.0637$, $wR_2 = 0.1295$	$R_1 = 0.0269$, $wR_2 = 0.0634$	$R_1 = 0.0503$, $wR_2 = 0.0999$	$R_1 = 0.0325$, $wR_2 = 0.0646$
Largest diff. peak and hole	1.037 and -0.533 $e. \text{Å}^{-3}$	0.341 and -0.436 $e. \text{Å}^{-3}$	0.58 and -0.44 $e. \text{Å}^{-3}$	0.42 and -0.31 $e. \text{Å}^{-3}$

Table S2: H-bond parameters of **1**.

Donor (D)	H atom	Acceptor (A)	Symmetry of A	D...H (in Å)	H...A (in Å)	D...A (in Å)	< D-H...A (indeg)
N4	H4	O2	x, 1+y, z	0.861(3)	1.903(2)	2.720(4)	158.05(19)
N2	H2	Cl4	1-x, 1+y, 1-z	0.860(3)	2.771(1)	3.476(3)	140.22(19)
C5	H5B	Cl3	-0.5+x, 1.5+y, z	0.960(5)	2.808(1)	3.724(5)	159.86(26)

Table S3: H-bond parameters of **2**.

Donor (D)	H atom	Acceptor (A)	Symmetry of A	D...H (in Å)	H...A (in Å)	D...A (in Å)	< D-H...A (in deg)
N4	H4	O2	1-x, 1+y, 1-z	0.861(1)	1.889(1)	2.700(2)	156.45(10)
N2	H2	Cl4	x, 1+y, z	0.860(1)	2.736(8)	3.435(2)	139.43(97)
C5	H5B	Cl3	1.5-x, 0.5+y, -z	0.959(3)	2.780(9)	3.694(3)	159.51(14)

Table S4: H-bonds parameters of **3**.

Donor (D)	H atom	Acceptor (A)	Symmetry of A	D...H (in Å)	H...A (in Å)	D...A (in Å)	< D-H...A (in deg)
N2	H2	O2	1-x, 1-y, 1-z	0.860(2)	1.929(2)	2.683(3)	145.68(16)
N3	H3T	O2	1-x, 1-y, 1-z	0.908(3)	1.814(3)	2.711(3)	168.45(25)
C23	H23B	Cl2	x, y, z	0.970(5)	2.673(2)	3.537(6)	148.63(31)
C11	H11B	Cl5	1-x, 1-y, 1-z	0.970(5)	2.759(1)	3.624(4)	148.77(24)
C7	H7A	Cl1	1-x, 1-y, -z	0.970(5)	2.868(1)	3.793(5)	159.89(26)
C9	H9A	Cl1	1-x, 1-y, -z	0.970(4)	2.809(1)	3.619(5)	141.53(24)
C18	H18C	Cl1	1-x, 1-y, -z	0.960(4)	2.836(1)	3.672(4)	146.16(24)
C9	H9A	O1	1-x, 1-y, -z	0.976(4)	2.823(3)	3.508(5)	128.36(25)

Table S5: H-bonds parameters of **4**.

Donor (D)	H atom	Acceptor (A)	Symmetry of A	D...H (in Å)	H...A (in Å)	D...A (in Å)	< D-H...A (indeg)
N2	H2	O2	1-x, 1-y, -z	0.860(3)	1.932(3)	2.695(5)	147.05(26)
N3	H3T	O2	1-x, 1-y, -z	0.913(4)	1.837(4)	2.737(4)	168.42(39)
C23	H23A	Cl4	x, y, z	0.970(3)	2.664(1)	3.530(3)	148.83(16)
C11	H11A	Cl1	1-x, 1-y, 1-z	0.970(3)	2.780(1)	3.599(3)	142.58(15)
C18	H18C	Cl1	1-x, 1-y, 1-z	0.960(3)	2.807(9)	3.601(3)	150.06(16)
C7	H7A	Cl1	1-x, 1-y, 1-z	0.970(3)	2.852(1)	3.776(3)	159.70(15)
C9	H9B	Cl5	x, y, z	0.970(2)	2.767(1)	3.620(3)	146.91(14)
C10	H10A	O2	1-x, 1-y, -z	0.960(3)	2.696(2)	3.410(3)	131.55(16)

Table S8. Coordination geometries, bond distances (Å) and bond angles (°) of **1**.

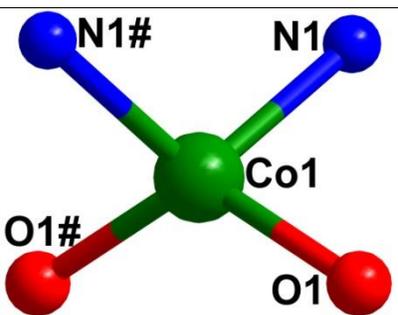
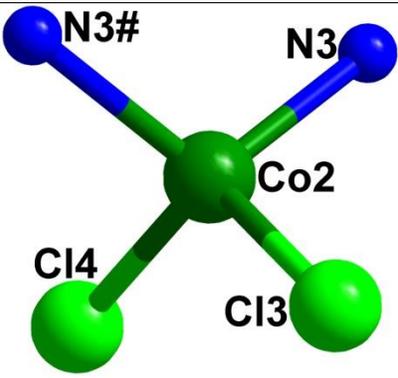
	Bond Distances (Å)	Bond Angles (°)	
 <p>Tetrahedral</p>	Co1-O1 1.921(2) Co1-O1# 1.921(2) Co1-N12.005(3) Co1-N1# 2.005(3)	O1-Co1-O1# 123.76(14) O1-Co1-N1 118.26(11) O1#-Co1-N1# 118.26(11) N1-Co1-N1# 109.56(17)	
 <p>Tetrahedral</p>	Co2-N3 2.030(3) Co2-N3# 2.030(3) Co2-Cl3 2.238 (2) Co2-Cl4 2.282(2)	N3-Co2-N3# 112.16(17) N3-Co2-Cl3 110.91(9) N3#-Co2-Cl3 110.91(9) N3#-Co2-Cl4 102.30(9) Cl3-Co2-Cl4 117.79(6)	

Table S9. Coordination geometries, bond distances (Å) and bond angles (°) of **2**.

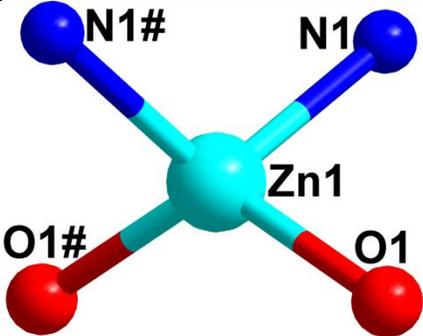
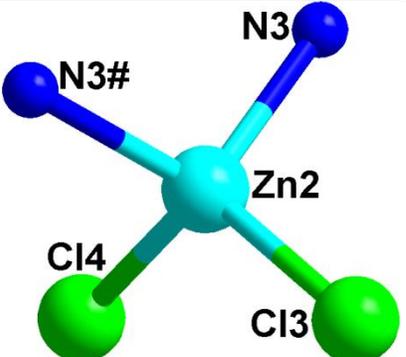
	Bond Distances (Å)	Bond Angles (°)
 <p>Tetrahedral</p>	Zn1-N1 1.998(1) Zn1-N1# 1.998(1) Zn1-O1 1.916(1) Zn1-O1# 1.916(1)	O1-Zn1-O1# 122.67(7) O1-Zn1-N1 116.79(5) O1-Zn1-N1 116.80(5) N1-Zn1-N1# 111.39(9)
 <p>Tetrahedral</p>	Zn2-N3 2.035(2) Zn2-N3# 2.035(2) Zn2-Cl3 2.216(9) Zn2-Cl3# 2.216(9)	N3-Zn2-N3# 109.41(8) N3-Zn2-Cl3 112.46(4) N3#-Zn2-Cl3 112.46(4) N3-Zn2-Cl4 101.85(4) N3#-Zn2-Cl4 101.85(4) Cl3-Zn2-Cl4 117.78(3)

Table S10. Coordination geometries, bond distances (Å) and bond angles (°) of **3**.

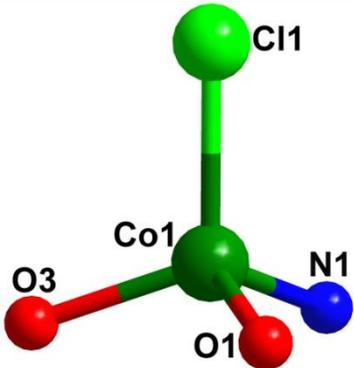
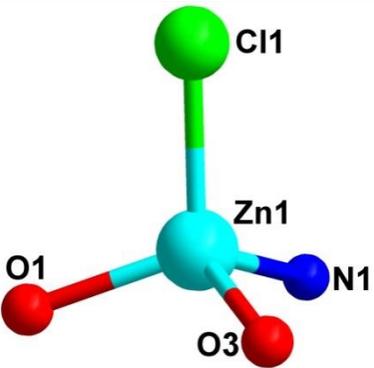
	Bond Distances (Å)	Bond Angles (°)
 <p>Tetrahedral</p>	Co1-O1 1.938(3) Co1-O3 1.956(3) Co1-N1 2.027(3) Co1-Cl1 2.260(1)	O1-Co1-O3 107.84(12) O1-Co1-N1 113.92(12) O3-Co1-N1 108.61(12) O1-Co1-Cl1 109.17(9) O3-Co1-Cl1 109.77(9) N1-Co1-Cl1 107.48(9)

Table S11. Coordination geometries, bond distances (Å) and bond angles (°) of **4**.

	Bond Distances (Å)	Bond Angles (°)
 <p>Tetrahedral</p>	Zn1-O1 1.932(2)	O1-Zn1-O3 107.42(7)
	Zn1-O3 1.953(2)	O1-Zn1-N1 111.89(7)
	Zn1-N1 2.017(2)	O3-Zn1-N1 109.72(7)
	Zn1-Cl1 2.244(9)	O1-Zn1-Cl1 109.08(6)
		O3-Zn1-Cl1 110.28(6)
		N1-Zn1-Cl1 108.45(6)