Electronic supplementary materials *Mendeleev Commun.*, 2019, **29**, 643–645

Synthesis, crystal structures and solid state reactions of zinc(II) cyclobutane-1,1′-dicarboxylates containing 1,2-bis(pyrid-4-yl)ethylene

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Synthesis

General. Complexes **1** and **2** were obtained by slow mixing of solutions. Commercially available reagents were used as received, in particular, $Zn(NO_3)_2 \cdot 6H_2O$ (Chimmed, Russia, «pure»), $Zn(OAc)_2 \cdot 2H_2O$ (Roth, Germany, 99%), cyclobutane-1,1-dicarboxylic acid (Acros organics, 99%), 1,2-bis(4-pyridyl)ethylene (Sigma Aldrich, Germany, 97%). IR spectra were measured using a Perkin–Elmer Spectrum 65 instrument by the attenuated total reflection (ATR) method in the range 4000–400 cm^{-1}. CHN analysis was performed by using an automatic CHNS analyzer EuroEA3000 at the Center of Collective Use of IGIC RAS.

*Complex **1***: An aqueous solution (10 ml) of $Zn(NO_3)_2 \cdot 6H_2O$ (0.030 g, 0.10 mmol) and cyclobutane-1,1-dicarboxylic acid (0.014 g, 0.10 mmol) was placed at the bottom of a test tube. Then, a H_2O/MeCN interphase (4/4 ml) was carefully layered. An acetonitrile solution (10 ml) of 1,2-bis(pyrid-4-yl)ethylene (0.037 g, 0.20 mmol) was carefully added on the top. The test tube was covered and allowed to stand at room temperature for nine days. The resulting colorless crystals were suitable for X-ray diffraction analysis. Crystals were filtered, washed with water, and dried in air at room temperature. IR-spectrum (ATR method), ν/cm^{-1}: 3555 w, 3478 w, 3377 w, 3275 w, 3098 w, 3085 w, 3053 w, 2980 w, 2951 w, 2931 w, 2857 w, 1615 m, 1591 m, 1509 m, 1433 m, 1350 s, 1305 m, 1257 m, 1217 m, 1162 m, 1114 m, 1073 m, 1029 m, 986 m, 962 m, 922 m, 899 m, 871 m, 829 s, 769 m, 736 m, 710 m, 651 m, 604 m, 574 s, 543 s, 508 s, 492 s, 463 , 447 s, 421 s. Calculated (%) for $C_{18}H_{18}N_2O_5Zn$: %: C, 53.02; H, 4.45; N, 6.87; found (%): C, 53.81; H, 4.78; N, 7.40. The yield of **1** was 0.0166 g (40.3 % counting per Zn).

*Complex **2*** was obtained in a mixture with **1** *via* a procedure similar to that used in the synthesis of pure complex **1**. Amounts of reagents: aqueous solution (15 ml) of $Zn(OAc)_2 \cdot 2H_2O$ (0.030 g, 0.14 mmol) and cyclobutane-1,1-dicarboxylic acid (0.020 g, 0.14 mmol), H_2O/MeCN interphase (2/4 ml), acetonitrile solution (10 ml) of bis(4-pyridyl)ethylene (0.122 g, 0.67 mmol). The colorless crystals were grown after a week.

After irradiation of single crystals of **1** for 8 h with Xe laser (λ = 365 nm; 200 W source operating at 40 % of the full intensity), complex $[Zn(bpe)(cbdc)]_{0.5}[Zn_2(tpcb)(cbdc)_2]_{0.25} \cdot 0.5H_2O$ (**4**) was obtained.

Descriptors of intermolecular interactions between olefin bonds in 1 and 3.

Figure S1 shows the mentioned descriptors. In the ideal case: $\theta = 0^o$, θ_1 (the angle between the meanplanes of the parallelogram formed by olefin bonds and a molecule) = 90^o, and θ_2 (the obtuse angle of the parallelogram formed by olefin bonds) = 90^o.[S1]

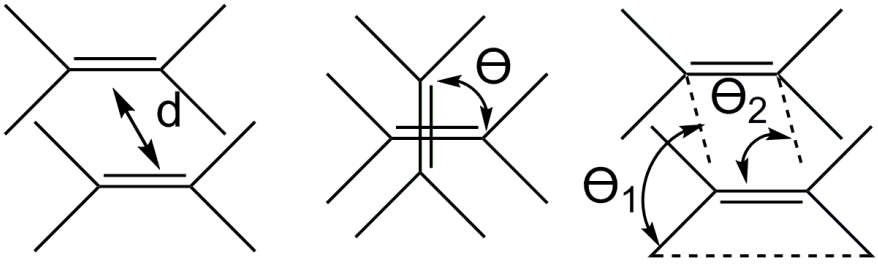


Figure S1 Schematic presentation of descriptors.

Table S1 Geometry of intermolecular interactions in [Zn(bpe)(cbdc)]·H_2O **(1)** and [Zn(bpe)(Me_2mal)]·H_2O **(3)**.

	d/Å	Θ/deg	Θ_1/deg	Θ_2/deg
1	4.28	29	67	80
3	4.14	28	77	80

^{1}H NMR analysis of acidified 1 and 4 in DMSO-d_6

^{1}H NMR spectra were recorded on a 400 MHz Varian INOVA 400 FT-NMR spectrometer. All the samples were dissolved at room temperature with a drop of HNO_3 added.

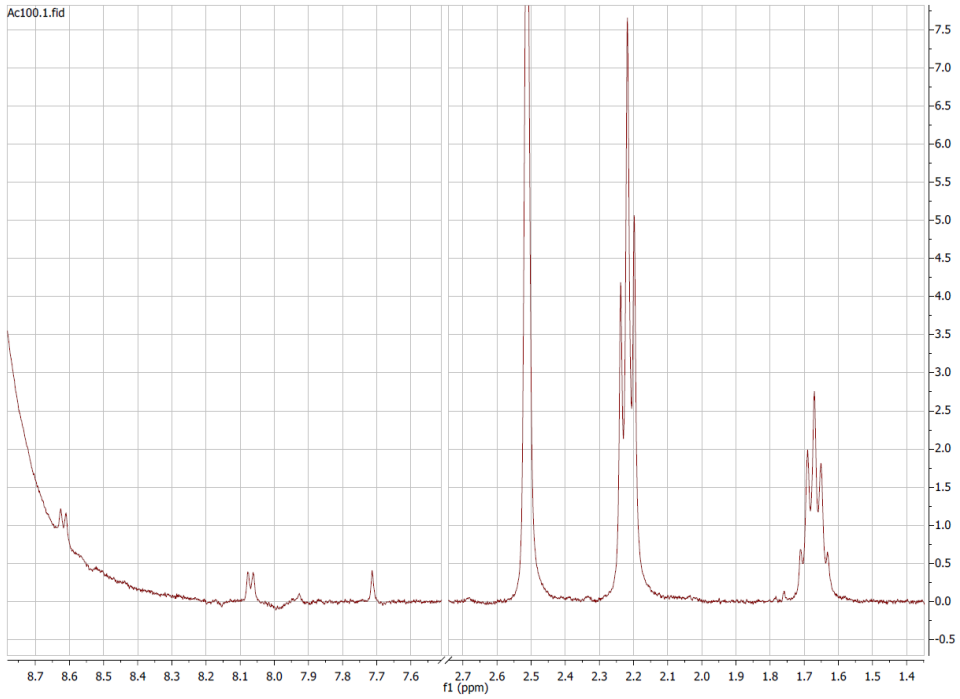


Figure S2 ^{1}H NMR spectrum of complex **1**.

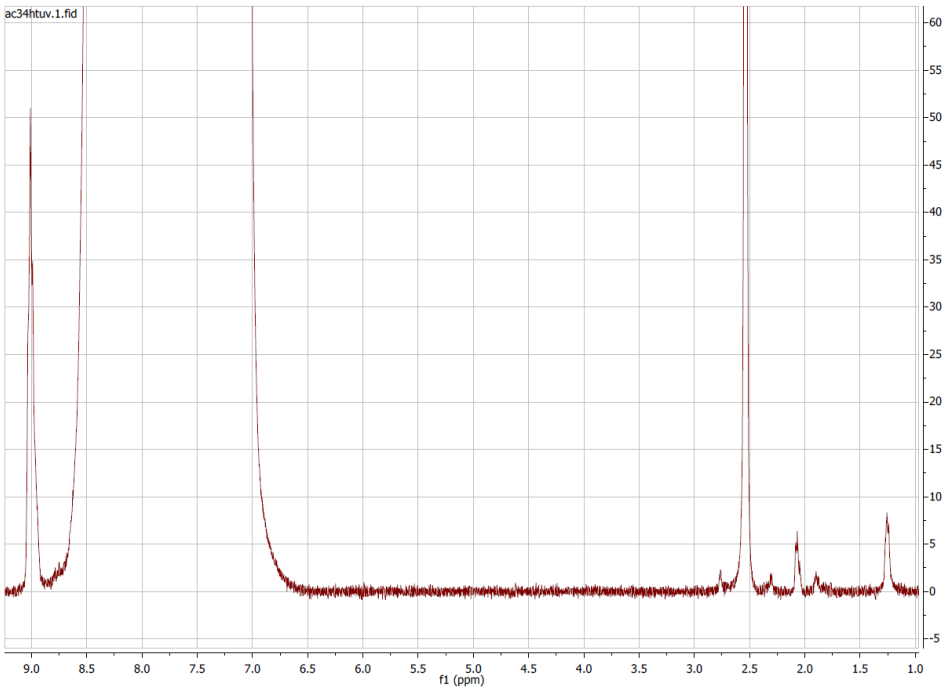


Figure S3 ^{1}H NMR spectrum of complex **3**.

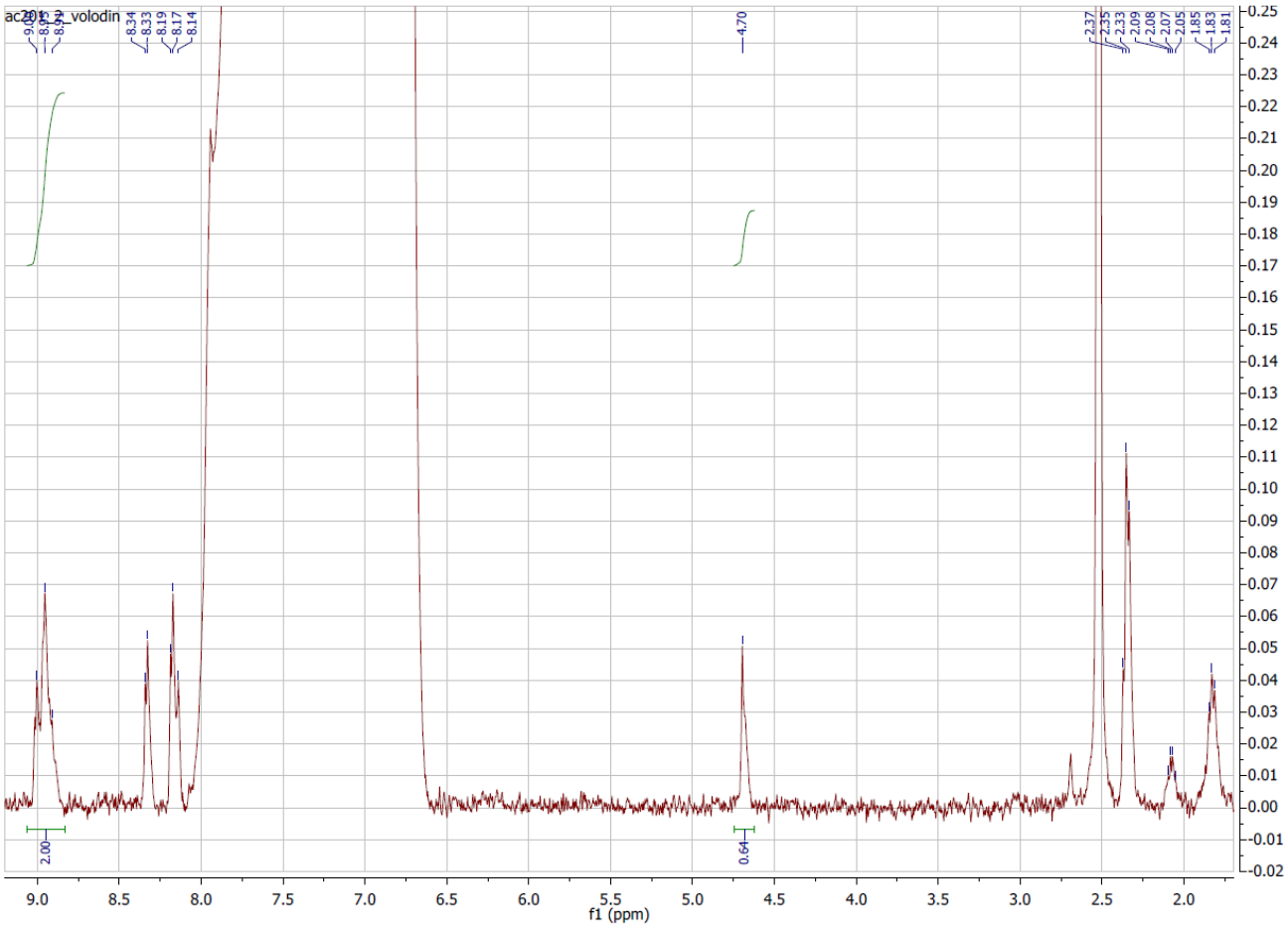


Figure S4 ^{1}H NMR spectrum of **1** irradiated for 8 h.

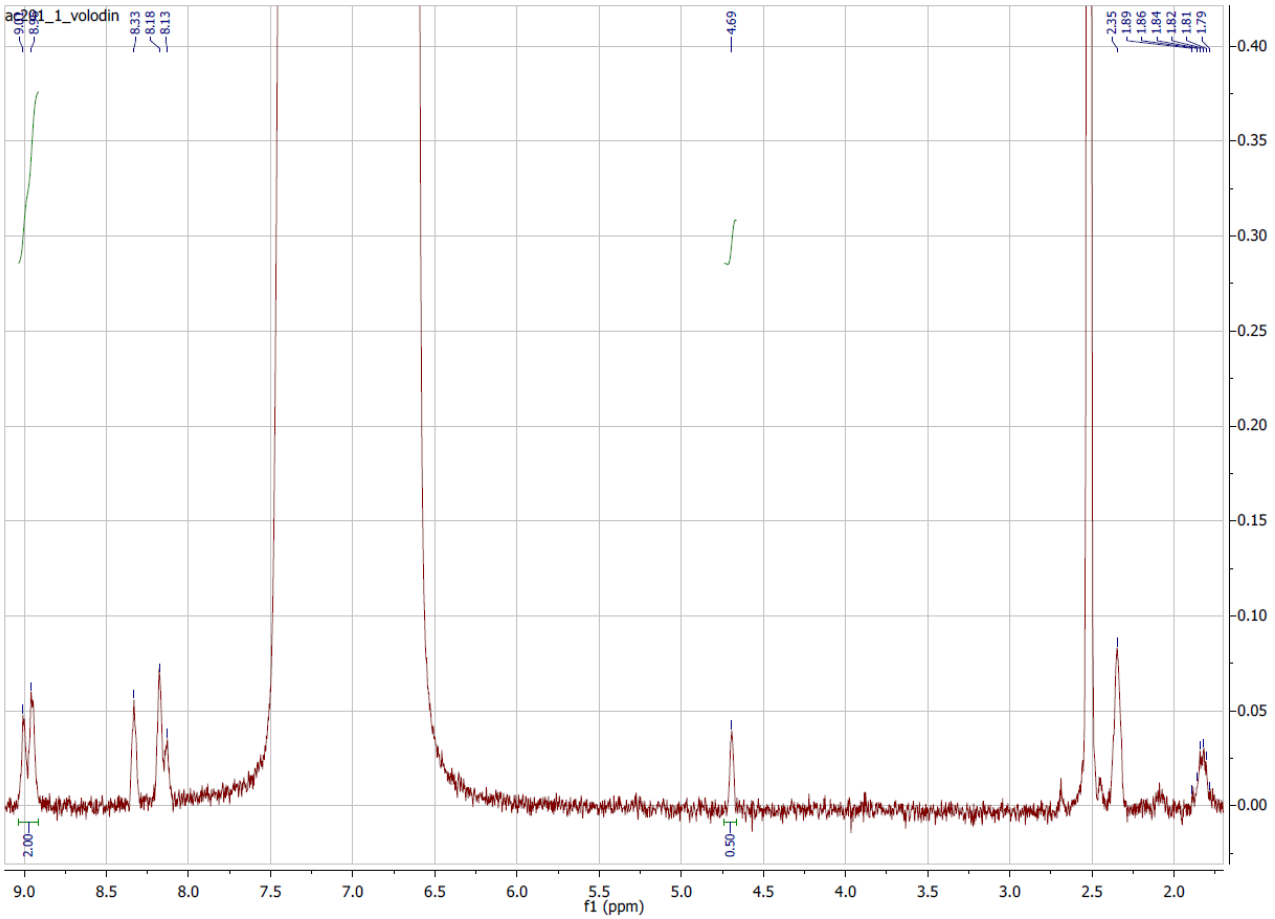


Figure S5 ^{1}H NMR spectrum of **1** heated for 3 h and irradiated for 8 h.

Powder X-Ray diffraction

Powder patterns were recorded at room temperature on a Bruker D8 Advance diffractometer equipped with a LynxEye detector and a Ge(111) monochromator at $\lambda(CuK\alpha_1)$ = 1.54060 Å and θ/2θ scans in 2θ range of 4–60°. The powder patterns were modeled within the Rietveld method using Bruker TOPAS4.2 software.[S2] Fundamental parameters approach[S3] was used for profile fitting. Preferred orientation of crystallites was taken into account with the spherical harmonics approach.[S4] In all the cases, only the background, parameters of microstructure, preferred orientation and unit cell parameters were refined while atomic coordinates were fixed on the values obtained with the corresponding single-crystal experiments.

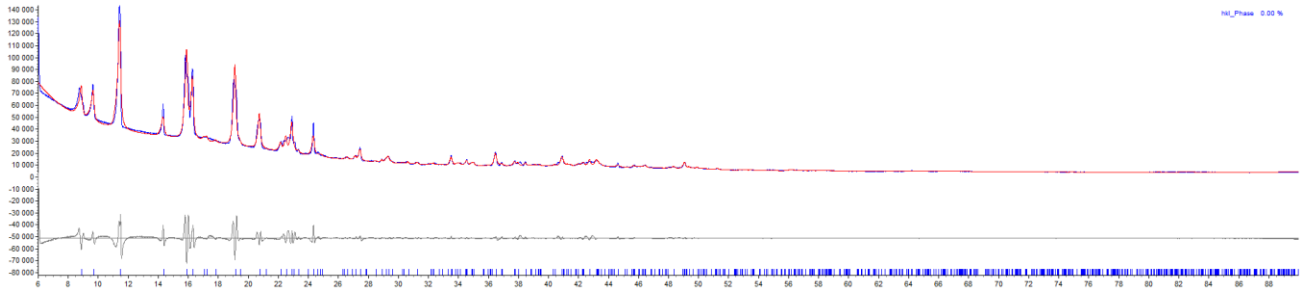


Figure S6 The experimental (blue) and calculated (red) powder patterns for $[Zn(bpe)(Me_2mal)]_2[Zn_2(tpcb)(Me_2mal)_2]\cdot H_2O$ (complex **3** heated at 120° for 3 h and irradiated for 8 h) and their difference (grey). R_{wp}/R_{bragg} = 6.79/1.00 % indicate purity of the sample.

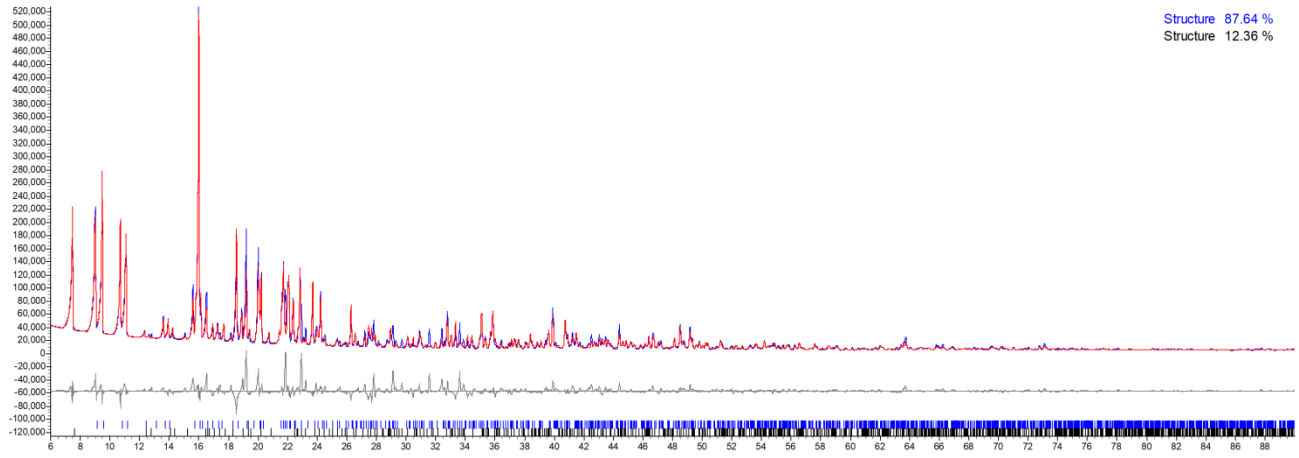


Figure S7 The experimental (blue) and calculated (red) powder patterns for a mixture of $[Zn(bpe)(cbdc)] \cdot H_2O$ (**1**) and $[Zn_2(H_2O)_2(bpe)cbdc_2]_n$ (**2**) as obtained from zinc(II) acetate and their difference (grey).

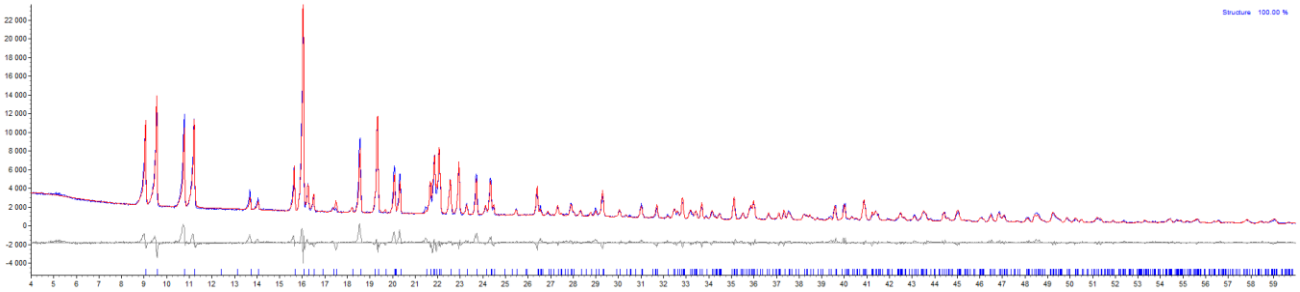


Figure S8 The experimental (blue) and calculated (red) powder patterns for [Zn(*bpe*)(cbdc)] · H_2O (**1**) and their difference (grey). R_{wp}/R_{bragg} = 8.87/6.34 % indicate purity of the sample.

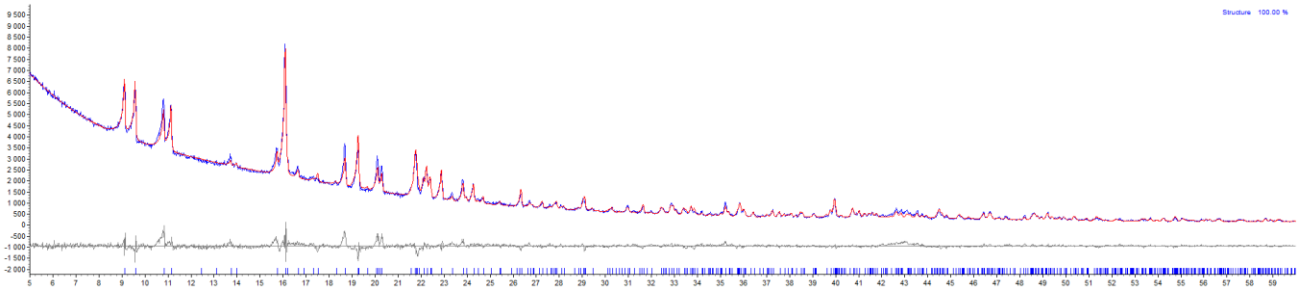


Figure S9 The experimental (blue) and calculated (red) powder patterns for sample **1** heated at 120° for 3 h and their difference (grey). R_{wp}/R_{bragg} = 5.63/4.78 % indicate purity of the sample.

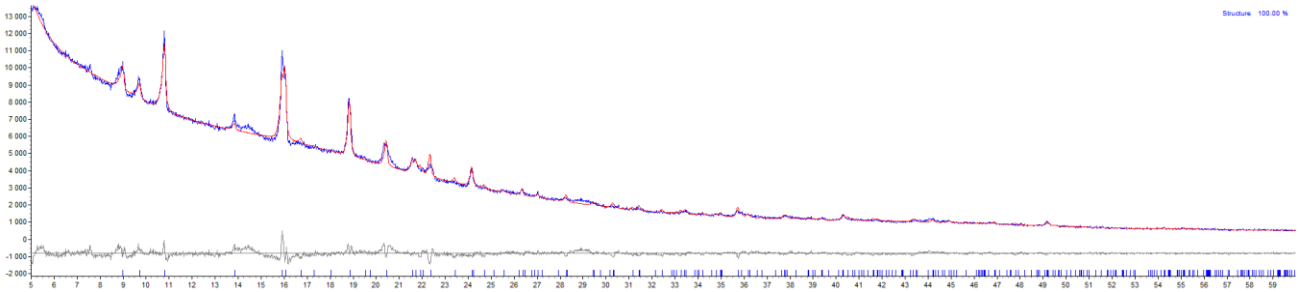


Figure S10 The experimental (blue) and calculated (red) powder patterns for [Zn(bpe)cbdc]$_2$[Zn_2(tpcb)$cbdc_2$]·H_2O (**4**) (complex **1** irradiated for 8 h) and their difference (grey). R_{wp}/R_{bragg} = 3.28/0.82 % indicate purity of the sample.

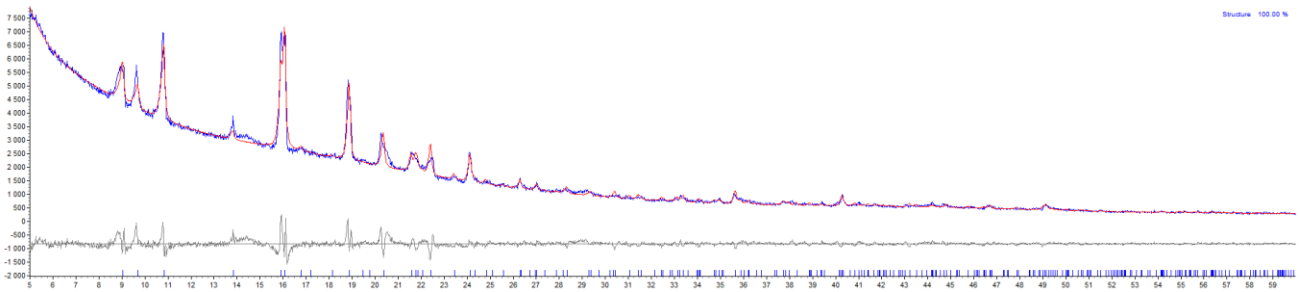


Figure S11 The experimental (blue) and calculated (red) powder patterns for [Zn(bpe)cbdc]$_2$[Zn$_2$(tpcb)cbdc$_2$]·H$_2$O (**4**) (complex **1** heated at 120° for 3 h and irradiated for 8 h) and their difference (grey). R_{wp}/R_{bragg} = 5.26/2.47 % indicate purity of the sample.

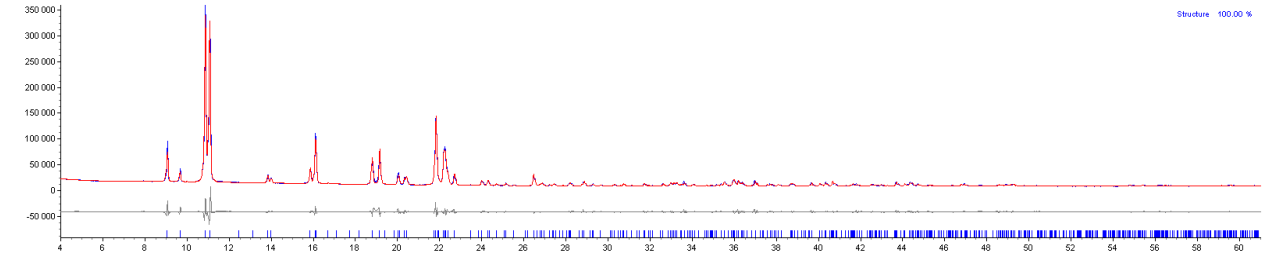


Figure S12 The experimental (blue) and calculated (red) powder patterns for [Zn(*bpe*)(Me$_2$mal)] · H$_2$O (**3**) and their difference (grey). R_{wp}/R_{bragg} = 6.04/1.42 % indicate purity of the sample.

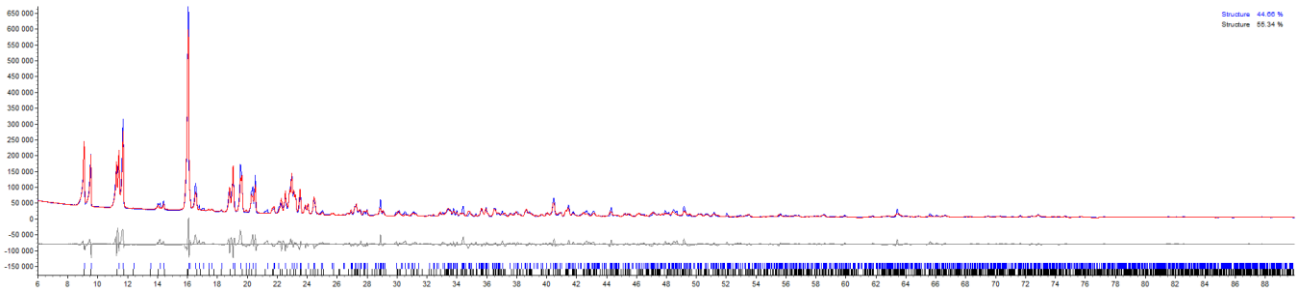
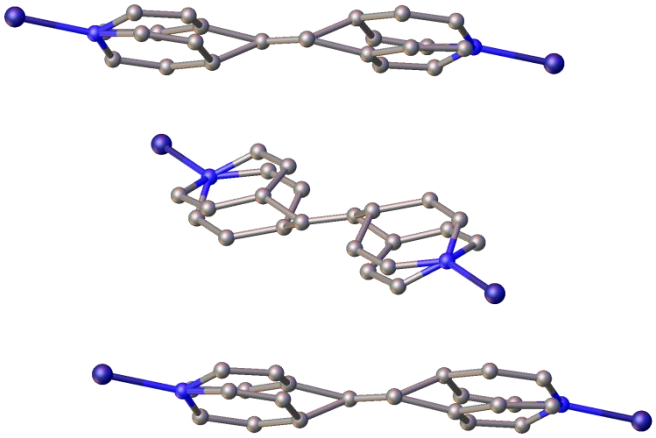


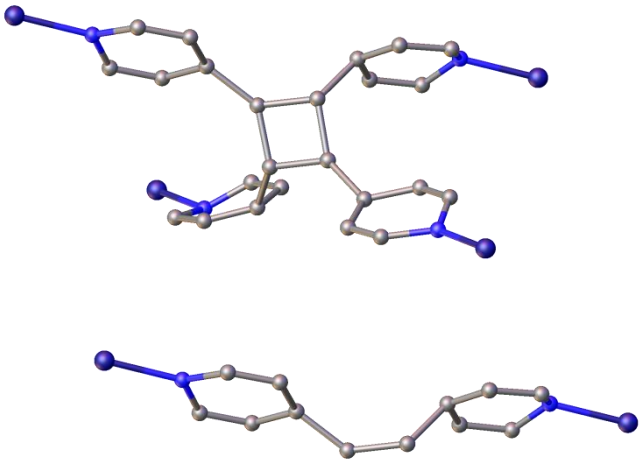
Figure S13 The experimental (blue) and calculated (red) powder patterns for [Zn(*bpe*)(Me$_2$mal)] · H$_2$O (**3**) heated at 120° for 3 h and their difference (grey). R_{wp}/R_{bragg} = 16.5/3.53 % indicates that the sample consists of two phases. Two $P2_1/c$ phases with similar crystal parameters describe the pattern best of all.

Fragment of crystal packing of 4.

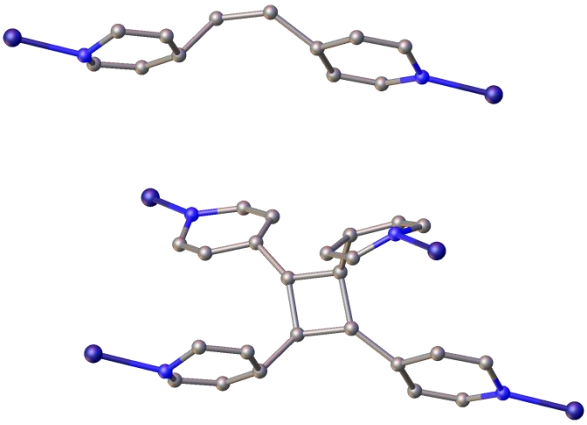
For all cases the same six metal atoms (violet) and different positions of the disordered linker are depicted (top, three bpe molecules; middle and bottom, 1.5 tpcb molecules).



bpe-containing moieties in the crystal of $[Zn(bpe)(cbdc)]_{0.5}[Zn_2(tpcb)(cbdc)_2]_{0.25}\cdot 0.5H_2O$



tpcb-containing moieties in the crystal of $[Zn(bpe)(cbdc)]_{0.5}[Zn_2(tpcb)(cbdc)_2]_{0.25}\cdot 0.5H_2O$. One of two equally disordered positions.



tpcb-containing moieties in the crystal of $[Zn(bpe)(cbdc)]_{0.5}[Zn_2(tpcb)(cbdc)_2]_{0.25}\cdot 0.5H_2O$. The second of two equally disordered positions.

SYSTRE input files for underlying nets of complexes 1 and 2

crystal

name 1

cell 8.5212 10.5292 21.8613 90.000 117.550 90.000

group P121/c1

atom 1 2 0.94668 0.49534 0.68300

edge 1 1.0533 -0.0047 0.8170

edge 1 1.0533 0.9953 0.8170

end

---

crystal

name 2

cell 7.2295 23.0800 10.6360 90.000 135.420 90.000

group P121/c1

atom 1 3 0.24230 0.19196 0.39954

edge 1 0.5047 0.2780 0.3975

edge 1 -0.4953 0.2220 -0.1025

edge 1 0.5047 0.2220 0.8975

atom 2 4 0.50474 0.27796 0.39747

edge 2 0.2423 0.1920 0.3995

edge 2 1.2423 0.3080 0.8995

edge 2 0.2423 0.3080 -0.1005

edge 2 -0.5047 0.7220 0.6025

end

References

S1 K. Gnanaguru, N. Ramasubbu, K. Venkatesan and V. Ramamurthy, *J. Org. Chem.*, 1985, **50**, 2337.

S2 *Bruker TOPAS 5 User Manual*, Bruker AXS GmbH, Karlsruhe, Germany, 2014.

S2 R.W. Cheary and A. Coelho, *J. Appl. Crystallogr.* 1992, **25**, 109.

S3 M. Järvinen, *J. Appl. Crystallogr.*, 1993, **26**, 525.