Supporting Information

Accordion and layer-sliding motion to produce anomalous thermal expansion behaviour in 2D-coordination polymers

Prem Lama,*[a] Arpan Hazra[b] and Leonard J. Barbour*[b]

[a]School of Chemical Sciences, Goa University, Taleigao Plateau, Taleigao 403206, Goa, India.
[b]Department of Chemistry and Polymer Science, University of Stellenbosch, Matieland 7602, Stellenbosch, South Africa

Synthesis

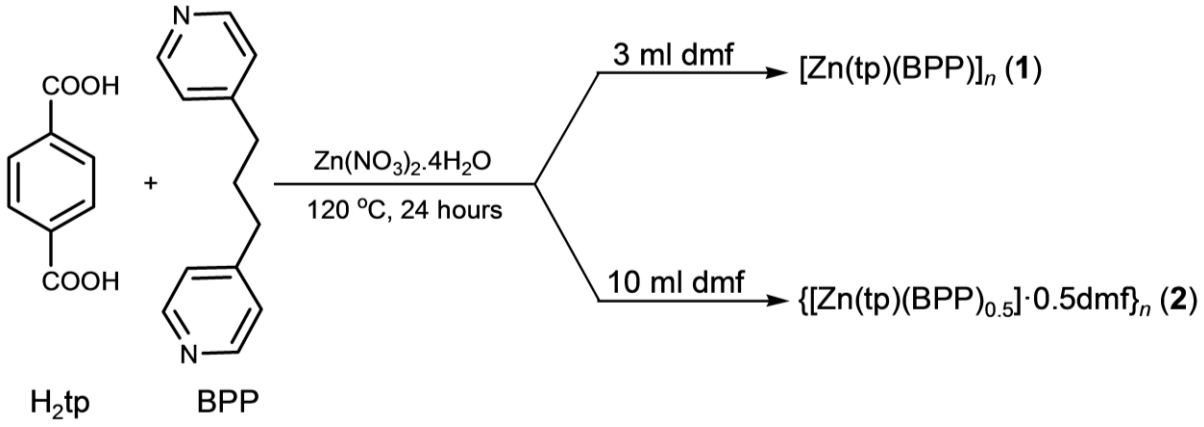
All chemicals and solvent used in these experiments were purchased from Aldrich and used without any further purification.

Synthesis of $[Zn(tp)(bpp)]_n$ (1)

A mixture of $Zn(NO_3)_2{\cdot}4H_2O$ (0.065 g, 0.25 mmol), terephthalic acid (0.049 g, 0.30 mmol) 1,3-bis(4-pyridyl)propane (0.035 g, 0.018 mmol) and 3 mL dmf (dmf = *N,N′*-dimethyl formamide) was sealed in a 20 mL screw-capped glass vial at 120 ^oC for 24 h to obtain block shaped light brown single crystals.

Synthesis of $\{[Zn(tp)(bpp)_{0.5}]{\cdot}0.5dmf\}_n$ (2)

A mixture of $Zn(NO_3)_2{\cdot}4H_2O$ (0.065 g, 0.25 mmol), terephthalic acid (0.049 g, 0.30 mmol) 1,3-bis(4-pyridyl)propane (0.035 g, 0.018 mmol) and 10 mL dmf was sealed in a 20 mL screw-capped glass vial at 120 ^oC for 24 h to obtain plate like colorless crystals. Crystals were washed few times with fresh dmf.



Scheme S1. Synthetic scheme for **1** and **2**.

Calculation of the coefficients of linear thermal expansion

The unit cell parameters of single crystals of **1** and **2** were determined at 20 K intervals respectively. The results of the measurements are summarised in Tables S1-S5. For **1**, these values were used to calculate the linear thermal expansion coefficient, α, for each of the axes *a*, *b* and *c* using the following equation:

$$\propto=\Delta L/(L_0\,\Delta T)$$

ΔL is the difference in length of the crystallographic axis, L_0 is the initial axis length at the initial temperature, T_0, and ΔT is the change in temperature. The volumetric expansion coefficient, αV, can be calculated using a modified form of the above equation, i.e. by substituting ΔV for ΔL and V_0 for L_0. The standard deviations for thermal expansion coefficients of **1** are calculated using the "propagation of measurement uncertainty" method.[1] The crystal mosaicity remains approximately the same for the different unit cell determinations. Since **2** crystallises in the monoclinic crystal system, the coefficients of thermal expansion were calculated using the program *PASCal*.[2]

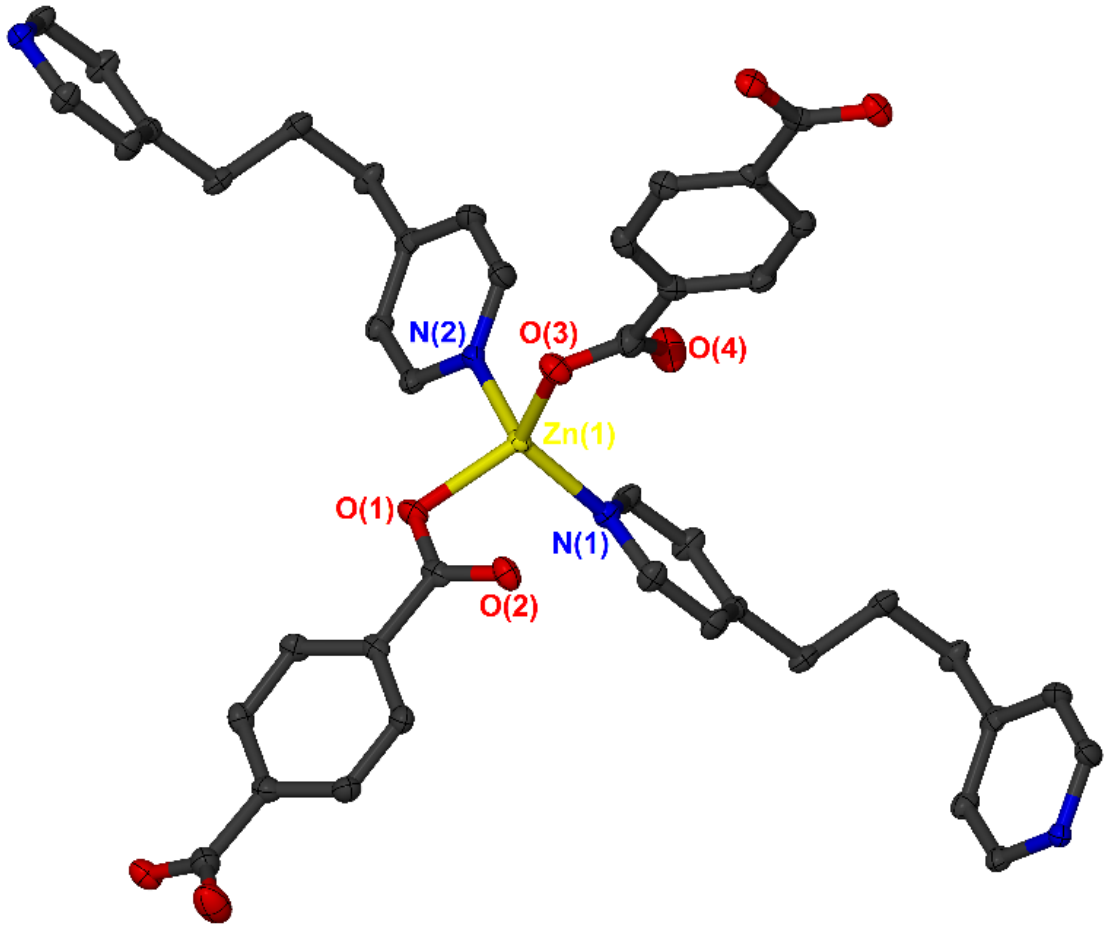


Figure S1. View of the coordination environment of Zn^{2+} in **1** (50% probability thermal ellipsoids; hydrogen atoms omitted for clarity).

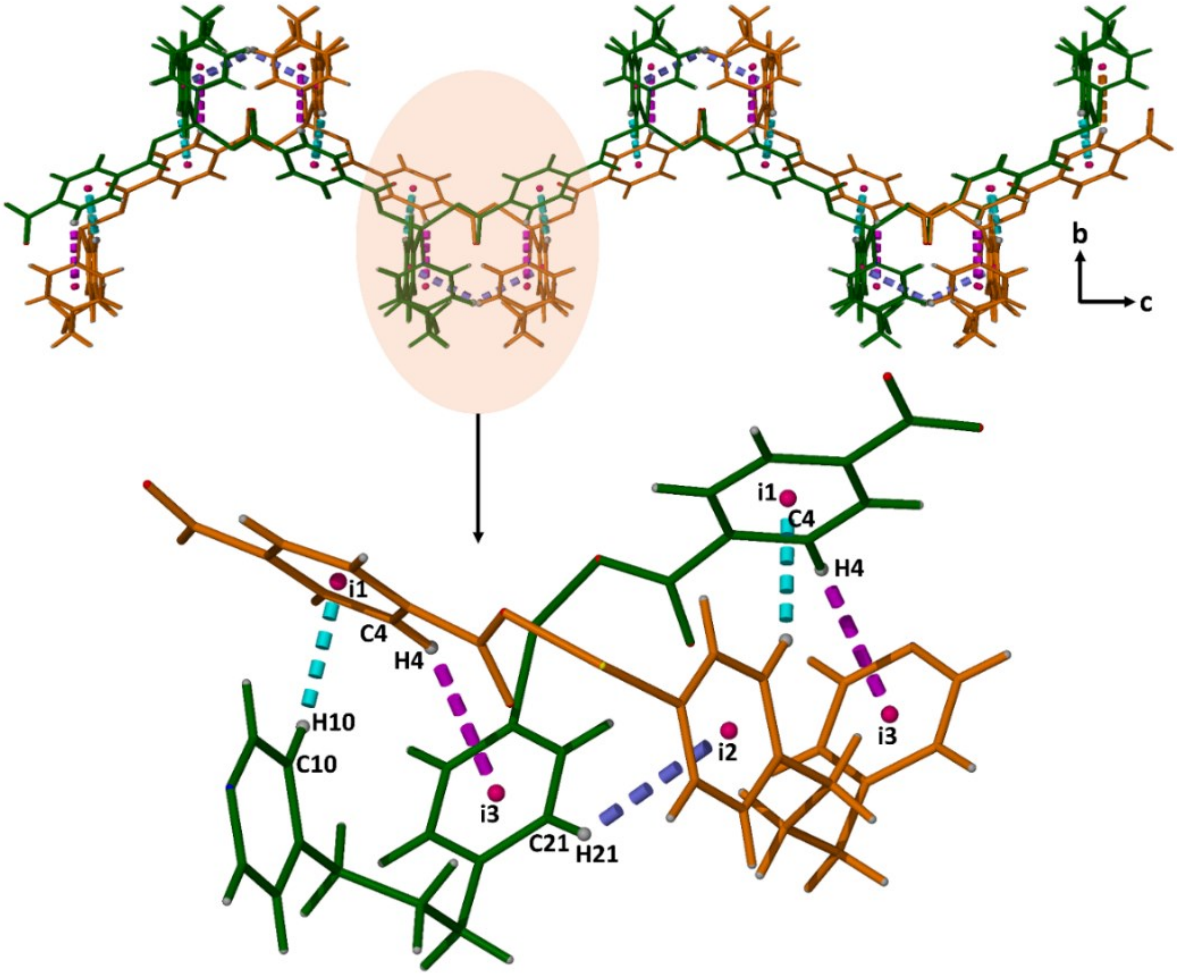


Figure S2. Top: the zig-zag interwoven layer (viewed along the *a* axis) with C-H···π interactions shown as dotted lines; Bottom: magnified view of the shaded area.

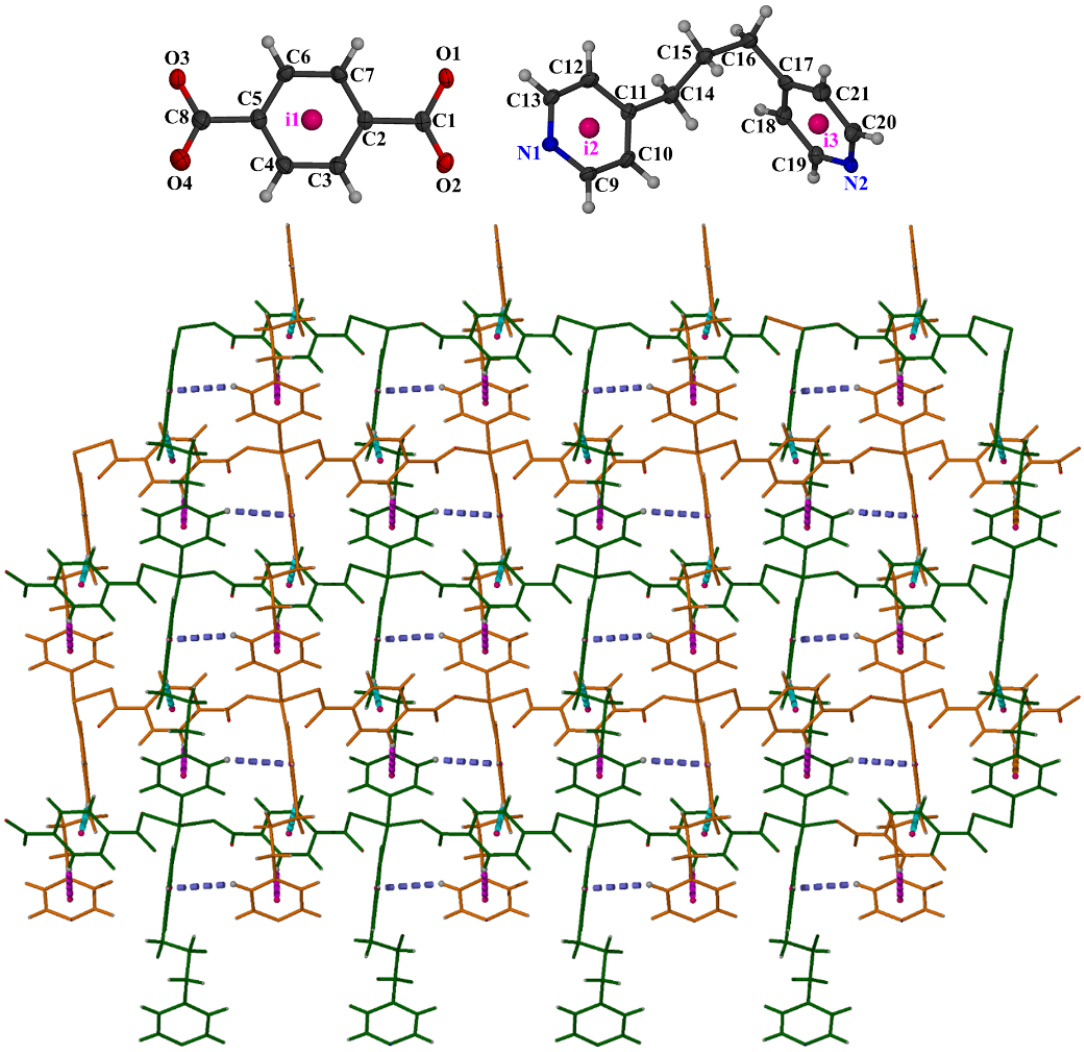


Figure S3. Perspective view showing the different C-H···π interactions between the interwoven layers in **1**.

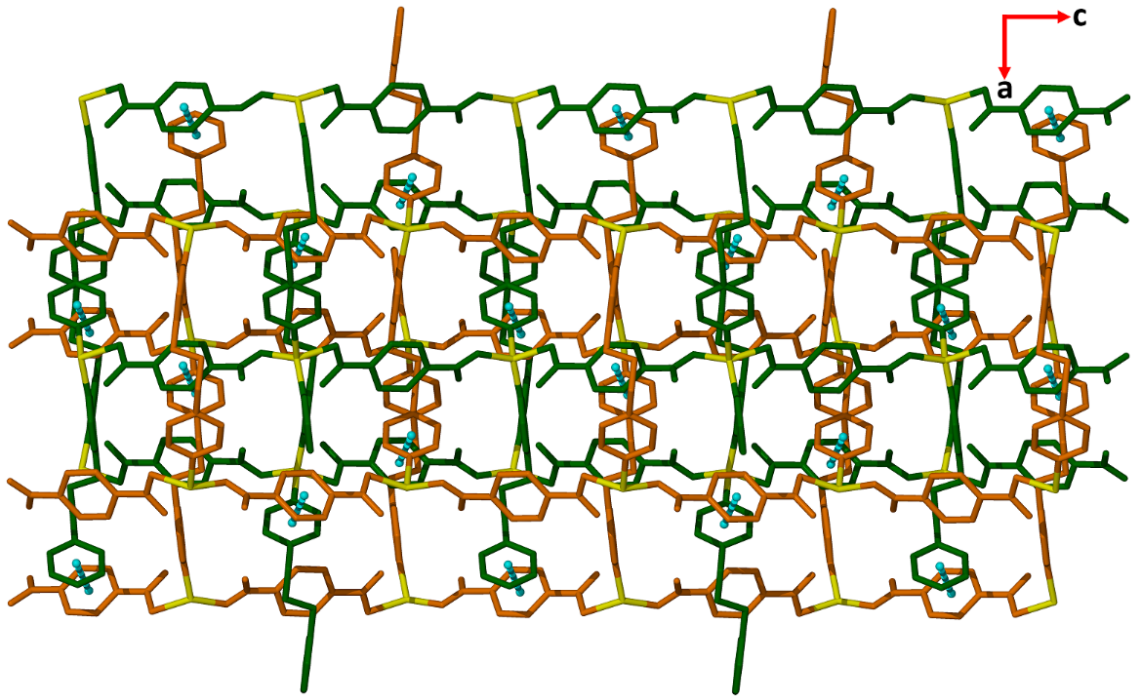


Figure S4. View along [010] showing the π···π interactions between the two interwoven sheets.

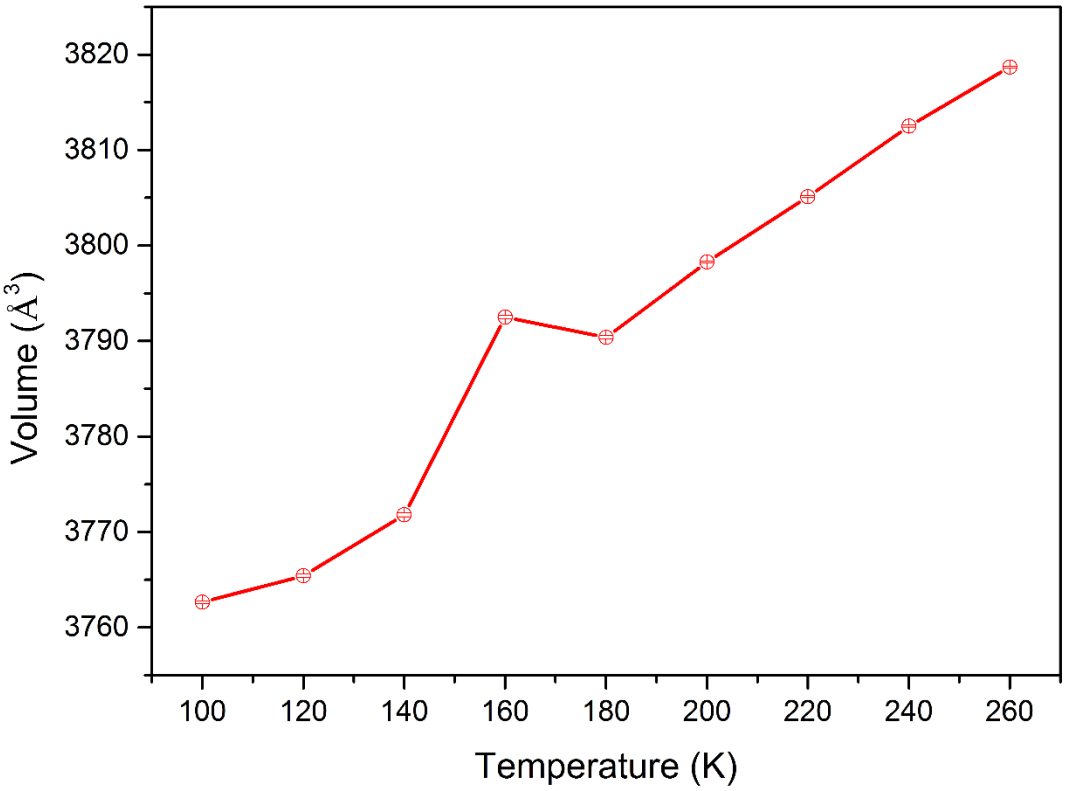


Figure S5. Variation of unit cell volume of **1** with temperature .

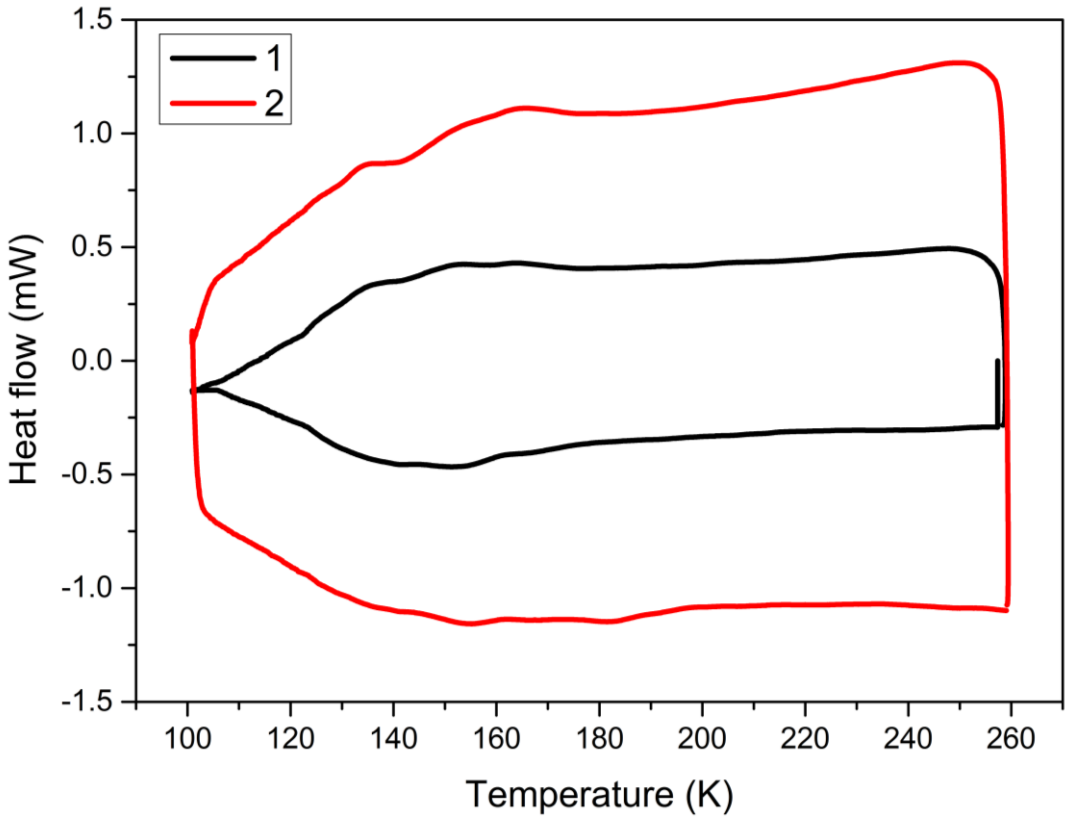


Figure S6. Differential scanning calorimetry (DSC) of **1** (black) and **2** (red).

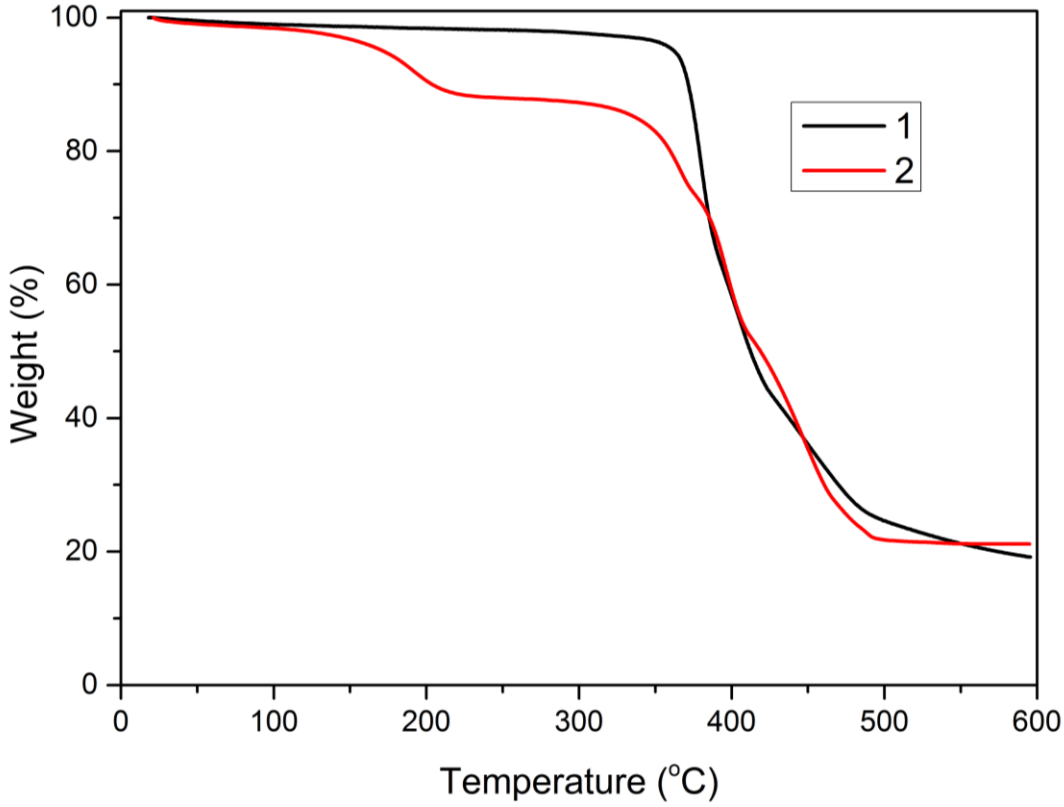


Figure S7. Thermogravimetric analysis (TGA) of **1** (black) and **2** (red).

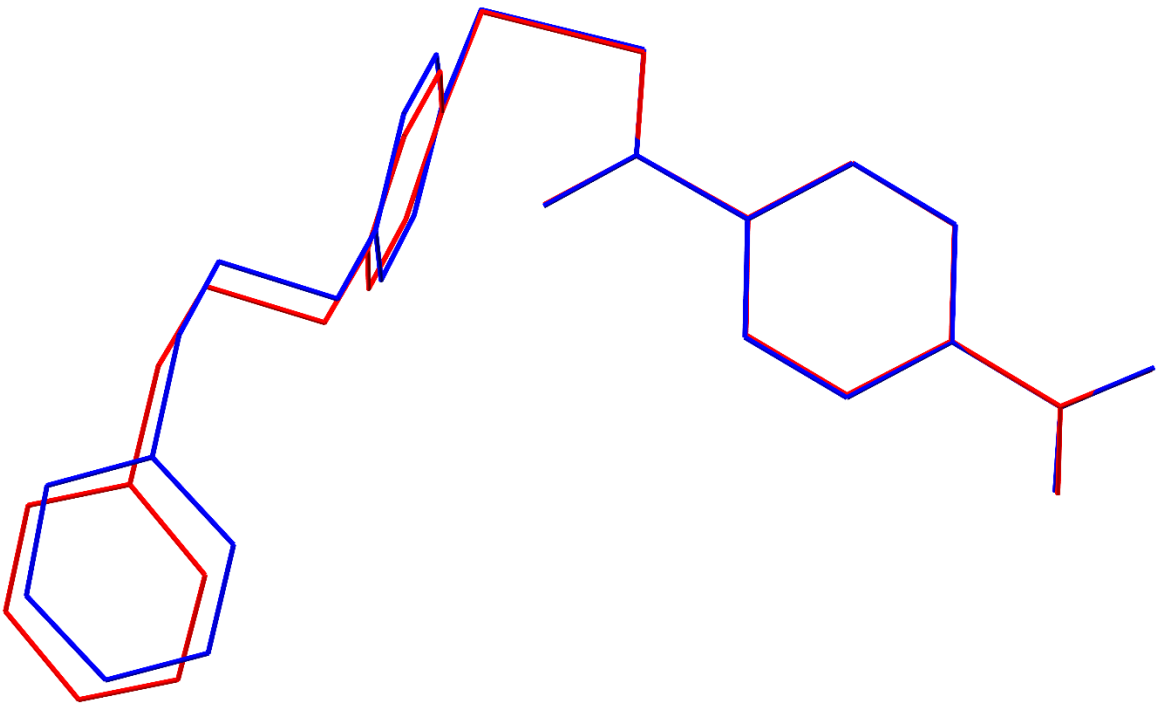


Figure S8. Poor overlap of the bpp unit in **1** at two different temperatures (blue, 100 K; red, 260 K).

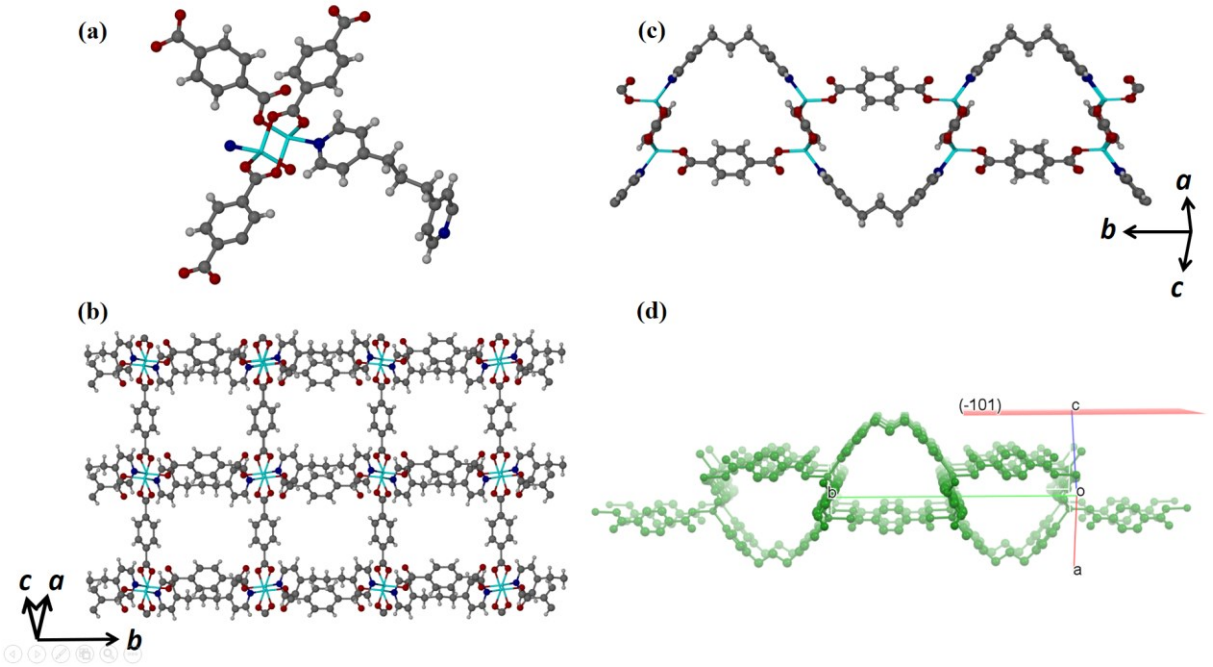


Figure S9: (a) Coordination environment of Zn^{2+} in **2**, (b) & (c) views of a single 2D layer in different direction, (d) view of a single 2D layer parallel to the (−101) plane.

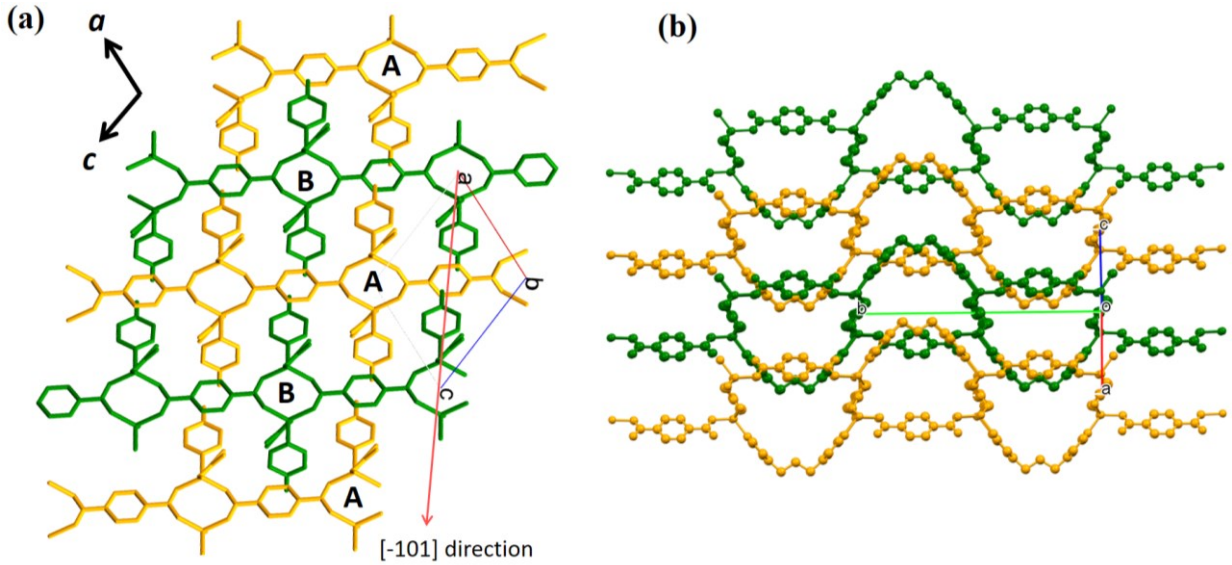


Figure S10: (a) Stacking of the 2D layers of **2** in *ABAB*.. fashion when viewed along [010] and (b) 3D supramolecular architecture formed by stacking of the 2D layers.

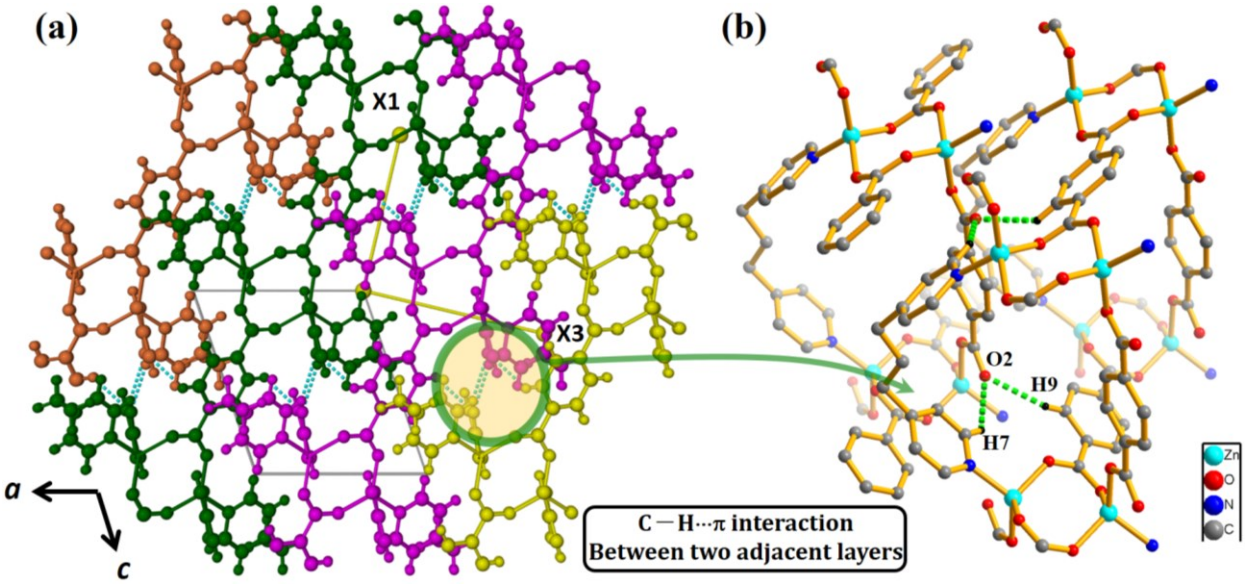


Figure S11: (a) Perspective view along [010] of compound **2** showing C-H···O interactions (dotted blue lines) between the adjacent 2D layers and (b) detailed view of the C-H···O interactions. (Hydrogen atoms except those participating in C-H···O bonding have been omitted for clarity.)

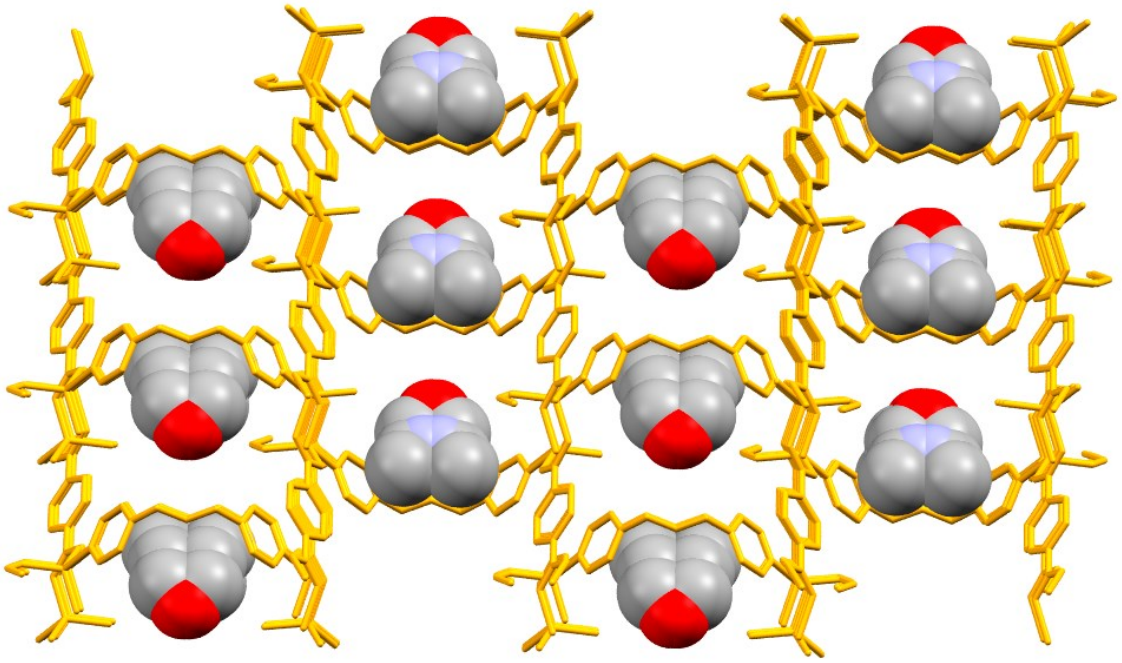


Figure S12: View along [001] of the 1D channels in compound **2**. The channel is filled with guest dmf (van der Waals surfaces) molecules.

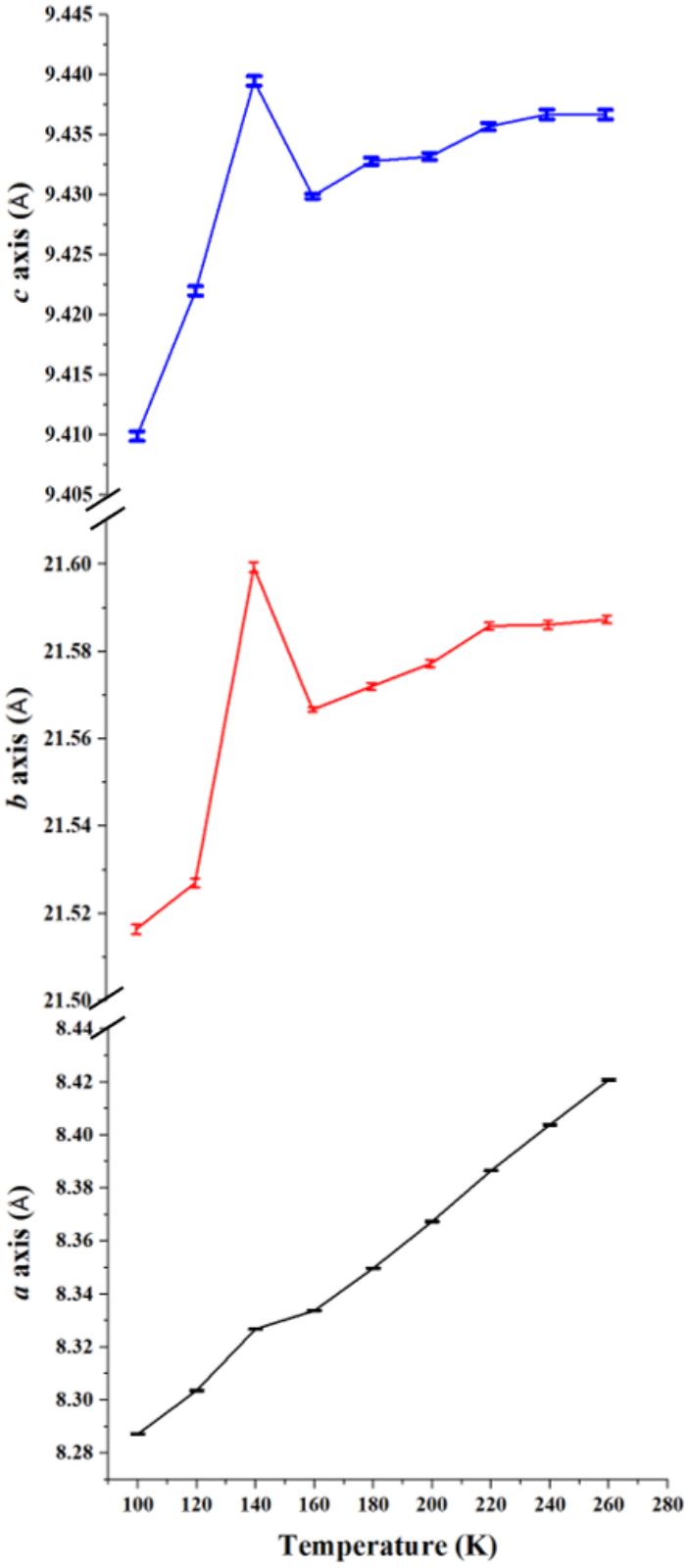


Figure S13: Variation of unit cell dimensions of compound **2** (including error bars) with temperature.

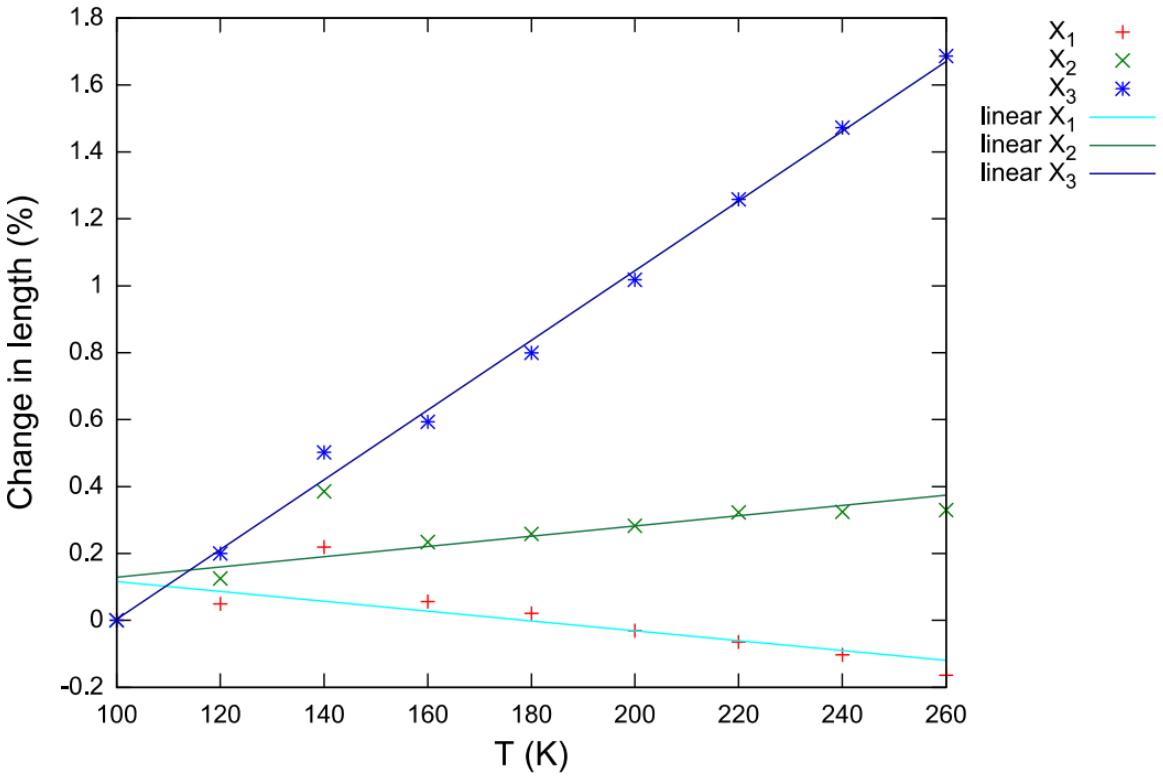
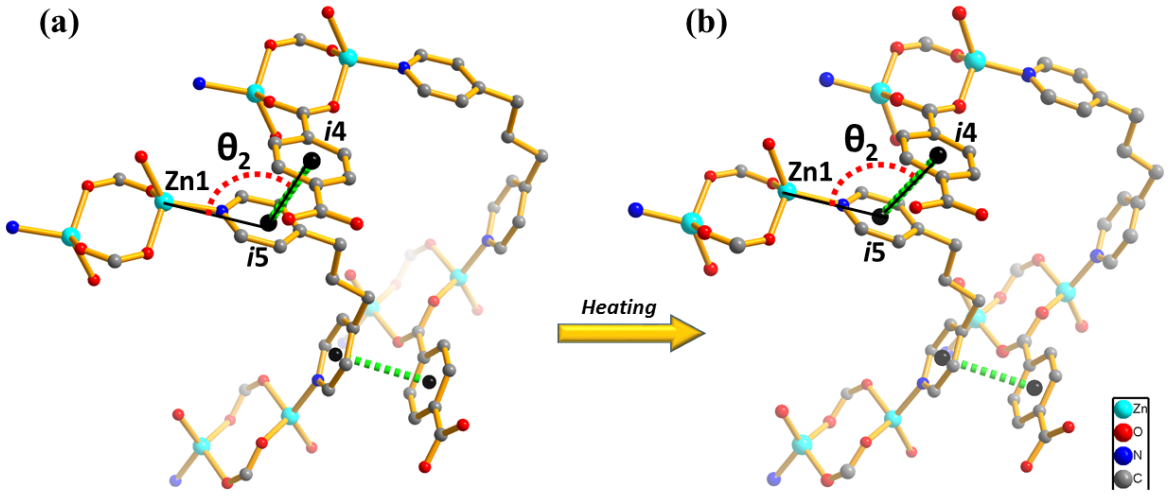


Figure S14: Percentage change in the principal axes in compound **2** with temperature.



	100 K	260 K
*i*4-*i*5	3.501(1) Å	3.552(1) Å
∠*i*4-*i*5-Zn1 (θ_2)	104.96(2)°	105.44(1)°

Figure S15: Detailed view of the $\pi\cdots\pi$ interactions between aromatic groups of carboxylate and pyridyl units at 100 K (a) and 260 K (b) in **2**.

Single Crystal X-ray Diffraction (SCXRD)

Experimental

Single crystal X-ray diffraction data for **1** were collected on a Bruker APEX-II Quasar CCD area-detector diffractometer equipped with an Oxford Cryosystems Cryostream 700Plus cryostat. For **2** data were collected on a Bruker D8 Venture with a Photon-2 area-detector diffractometer equipped with an Oxford Cryosystems Cryostream 800Plus series cryostat. Multilayer monochromators with $Mo_{K\alpha}$ radiation (λ = 0.71073 Å) from Incoatec $I_{\mu S}$ microsources weres used in both cases.

Data reduction was carried out by means of standard procedures using the Bruker software package SAINT[3] and absorption corrections and the correction of other systematic errors were performed using SADABS.[4] The structures were solved by direct methods using SHELXS-97 and refined using SHELXL-2016.[5] X-Seed[6] was used as the graphical interface for the SHELX program suite. Hydrogen atoms were placed in calculated positions using riding models.

Table S1. Crystallographic details for 1

Identification code	**1_260K**	**1_240K**	**1_220K**	**1_200K**	**1_180K**
Empirical formula	$C_{21}H_{18}N_2O_4Zn$	$C_{21}H_{18}N_2O_4Zn$	$C_{21}H_{18}N_2O_4Zn$	$C_{21}H_{18}N_2O_4Zn$	$C_{21}H_{18}N_2O_4Zn$
Formula weight	427.74	427.74	427.74	427.74	427.74
Temperature/K	260(2)	240(2)	220(2)	200(2)	180(2)
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	*Pbca*	*Pbca*	*Pbca*	*Pbca*	*Pbca*
a/Å	11.7522(19)	11.7500(18)	11.7459(17)	11.7438(17)	11.7422(17)
b/Å	16.5678(27)	16.5402(25)	16.5099(24)	16.4767(24)	16.4398(24)
c/Å	19.6125(31)	19.6170(30)	19.6217(29)	19.6295(29)	19.6352(28)
α/°	90	90	90	90	90
β/°	90	90	90	90	90
γ/°	90	90	90	90	90
Volume/Å^3	3818.71(11)	3812.51(10)	3805.11(10)	3798.29(10)	3790.37(19)
Z	8	8	8	8	8
ρ_{calc}g/cm^3	1.488	1.490	1.493	1.496	1.499
μ/mm^{-1}	1.316	1.318	1.321	1.323	1.326
F(000)	1760	1760	1760	1760	1760
Crystal size/mm^3	0.675 × 0.165 × 0.094	0.675 × 0.165 × 0.094	0.675 × 0.164 × 0.094	0.675 × 0.164 × 0.094	0.676 × 0.164 × 0.094
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
θ range for data collection/°	2.365 to 24.998	2.366 to 25.000	2.368 to 24.999	2.369 to 24.999	2.074 to 24.997
Index ranges	-13 ≤ h ≤ 13, -19 ≤ k ≤ 19, -23 ≤ l ≤ 23	-13 ≤ h ≤ 13, -19 ≤ k ≤ 19, -23 ≤ l ≤ 23	-13 ≤ h ≤ 13, -19 ≤ k ≤ 19, -23 ≤ l ≤ 23	-13 ≤ h ≤ 13, -19 ≤ k ≤ 19, -23 ≤ l ≤ 23	-13 ≤ h ≤ 13, -19 ≤ k ≤ 19, -23 ≤ l ≤ 23
Reflections collected	50353	50233	50062	50231	50128
Independent reflections	3331 [R_{int} = 0.0203, R_{sigma} = 0.0544]	3334 [R_{int} = 0.0204, R_{sigma} = 0.0535]	3328 [R_{int} = 0.0198, R_{sigma} = 0.0520]	3316 [R_{int} = 0.0196, R_{sigma} = 0.0508]	3319 [R_{int} = 0.0186, R_{sigma} = 0.0486]
Data/restraints/parameters	3331/0/253	3334/0/253	3328/0/253	3316/0/253	3319/0/253
Goodness-of-fit on F^2	1.116	1.096	1.108	1.086	1.080
Final R indexes [I>=2σ (I)]	R_1 = 0.0456, wR_2 = 0.0984	R_1 = 0.0449, wR_2 = 0.1004	R_1 = 0.0445, wR_2 = 0.1039	R_1 = 0.0431, wR_2 = 0.1019	R_1 = 0.0417, wR_2 = 0.1007
Final R indexes [all data]	R_1 = 0.0592, wR_2 = 0.1095	R_1 = 0.0585, wR_2 = 0.1129	R_1 = 0.0567, wR_2 = 0.1150	R_1 = 0.0544, wR_2 = 0.1127	R_1 = 0.0516, wR_2 = 0.1104
Largest diff. peak/hole / e Å^{-3}	0.770/-0.593	0.859/-0.651	0.833/-0.750	0.876/-0.759	0.880/-0.755
Mosaicity	0.37	0.38	0.37	0.37	0.37
CCDC number	1947067	1947066	1947065	1947064	1947063

Identification code	**1_160K**	**1_140K**	**1_120K**	**1_100K**	**1_260K-R**
Empirical formula	$C_{21}H_{18}N_2O_4Zn$	$C_{21}H_{18}N_2O_4Zn$	$C_{21}H_{18}N_2O_4Zn$	$C_{21}H_{18}N_2O_4Zn$	$C_{21}H_{18}N_2O_4Zn$
Formula weight	427.74	427.74	427.74	427.74	427.74
Temperature/K	160(2)	140(2)	120(2)	100(2)	260-R(2)
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	*Pbca*	*Pbca*	*Pbca*	*Pbca*	*Pbca*
a/Å	11.7573(12)	11.7402(16)	11.7441(32)	11.7519(21)	11.7508(17)
b/Å	16.4228(17)	16.3576(23)	16.3205(45)	16.2971(30)	16.5636(24)
c/Å	19.6413(21)	19.6405(27)	19.6453(54)	19.6460(34)	19.6111(28)
α/°	90	90	90	90	90
β/°	90	90	90	90	90
γ/°	90	90	90	90	90
Volume/Å^3	3792.50(17)	3771.79(19)	3765.41(18)	3762.64(12)	3817.02(10)
Z	8	8	8	8	8
ρ_{calc}g/cm^3	1.498	1.507	1.509	1.510	1.489
μ/mm^{-1}	1.325	1.332	1.335	1.336	1.317
F(000)	1760	1760	1760	1760	1760
Crystal size/mm^3	0.676 × 0.163 × 0.094	0.676 × 0.163 × 0.094	0.676 × 0.162 × 0.094	0.676 × 0.162 × 0.094	0.675 × 0.165 × 0.094
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
θ range for data collection/°	2.074 to 24.998	2.074 to 25.000	2.073 to 24.997	2.073 to 24.998	2.365 to 24.999
Index ranges	-13 ≤ h ≤ 13, -19 ≤ k ≤ 19, -23 ≤ l ≤ 23	-13 ≤ h ≤ 13, -19 ≤ k ≤ 19, -23 ≤ l ≤ 23	-13 ≤ h ≤ 13, -19 ≤ k ≤ 19, -23 ≤ l ≤ 23	-13 ≤ h ≤ 13, -19 ≤ k ≤ 19, -23 ≤ l ≤ 23	-13 ≤ h ≤ 13, -19 ≤ k ≤ 19, -23 ≤ l ≤ 23
Reflections collected	55211	50274	50637	50805	50376
Independent reflections	3320 [R_{int} = 0.0104, R_{sigma} = 0.0290]	3308 [R_{int} = 0.0173, R_{sigma} = 0.0452]	3303 [R_{int} = 0.0163, R_{sigma} = 0.0428]	3306 [R_{int} = 0.0164, R_{sigma} = 0.0425]	3338 [R_{int} = 0.0203, R_{sigma} = 0.0545]
Data/restraints/parameters	3320/0/253	3308/0/253	3303/0/253	3306/0/253	3338/0/253
Goodness-of-fit on F^2	1.063	1.096	1.092	1.079	1.134
Final R indexes [I>=2σ (I)]	R_1 = 0.0406, wR_2 = 0.1061	R_1 = 0.0366, wR_2 = 0.0920	R_1 = 0.0334, wR_2 = 0.0838	R_1 = 0.0304, wR_2 = 0.0748	R_1 = 0.0454, wR_2 = 0.1018
Final R indexes [all data]	R_1 = 0.0442, wR_2 = 0.1094	R_1 = 0.0449, wR_2 = 0.0996	R_1 = 0.0400, wR_2 = 0.0896	R_1 = 0.0362, wR_2 = 0.0793	R_1 = 0.0599, wR_2 = 0.1148
Largest diff. peak/hole / e Å^{-3}	0.963/-0.763	0.886/-0.613	0.787/-0.515	0.696/-0.416	0.769/-0.612
Mosaicity	0.37	0.37	0.38	0.38	0.37
CCDC number	1947062	1947061	1947060	1947059	1947068

Table S2. **Unit cell axes and volumes at variable temperatures for 1**.

***T* (K)**	***a* (Å)**	**St. dev.***	***b* (Å)**	**St. dev.***	***c* (Å)**	**St. dev.***	**V(Å^3)**	**St. dev.***	**Crystal mosaicity**
260	11.7522	0.0019	16.5678	0.0027	19.6125	0.0031	3818.71	0.11	0.37
240	11.7500	0.0018	16.5402	0.0025	19.6170	0.0030	3812.51	0.10	0.38
220	11.7459	0.0017	16.5099	0.0024	19.6217	0.0029	3805.11	0.10	0.37
200	11.7438	0.0017	16.4767	0.0024	19.6295	0.0029	3798.29	0.10	0.37
180	11.7422	0.0017	16.4398	0.0024	19.6352	0.0028	3790.37	0.19	0.37
160	11.7573	0.0012	16.4228	0.0017	19.6413	0.0021	3792.50	0.17	0.37
140	11.7402	0.0016	16.3576	0.0023	19.6405	0.0027	3771.79	0.19	0.37
120	11.7441	0.0032	16.3205	0.0045	19.6453	0.0054	3765.41	0.18	0.38
100	11.7519	0.0021	16.2971	0.0030	19.6460	0.0036	3762.64	0.12	0.38
260-R	11.7508	0.0017	16.5636	0.0024	19.6111	0.0028	3817.02	0.10	0.37

*Standard deviation calculated from unit cell refinement using the Apex III software suite.

Table S3. Crystallographic details for 2

Identification code	**2_260K**	**2_240K**	**2_220K**	**2_200K**	**2_180K**
Empirical formula	$C_{32}H_{29}N_3O_9Zn_2$	$C_{32}H_{29}N_3O_9Zn_2$	$C_{32}H_{29}N_3O_9Zn_2$	$C_{32}H_{29}N_3O_9Zn_2$	$C_{32}H_{29}N_3O_9Zn_2$
Formula weight	730.32	730.32	730.32	730.32	730.32
Temperature/K	2602)	240(2)	220(2)	200(2)	180(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/m$	$P2_1/m$	$P2_1/m$	$P2_1/m$	$P2_1/m$
a/Å	8.4208(4)	8.4039(4)	8.3866(3)	8.3674(3)	8.3498(3)
b/Å	21.5873(9)	21.5861(10)	21.5854(8)	21.5772(8)	21.5720(8)
c/Å	9.4367(4)	9.4367(4)	9.4357(3)	9.4332(3)	9.4328(3)
α/°	90	90	90	90	90

β/°	109.674(1)	109.586(1)	109.511(1)	109.423(1)	109.338(1)
γ/°	90	90	90	90	90
Volume/Å^3	1615.28(12)	1612.84(13)	1610.04(10)	1606.19(10)	1603.20(10)
Z	2	2	2	2	2
ρ_{calc}g/cm^3	1.502	1.504	1.506	1.510	1.513
μ/mm^{-1}	1.542	1.545	1.547	1.551	1.554
F(000)	748	748	748	748	748
Crystal size/mm^3	0.496 × 0.378 × 0.055	0.496 × 0.378 × 0.055	0.496 × 0.378 × 0.055	0.496 × 0.378 × 0.055	0.496 × 0.378 × 0.055
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
θ range for data collection/°	2.479 to 24.997	2.478 to 24.994	2.744 to 24.995	2.476 to 24.996	2.475 to 25.000
Index ranges	-10 ≤ h ≤ 10, -25 ≤ k ≤ 25, -11 ≤ l ≤ 10	-9 ≤ h ≤ 9, -25 ≤ k ≤ 25, -11 ≤ l ≤ 10	-9 ≤ h ≤ 9, -25 ≤ k ≤ 25, -11 ≤ l ≤ 10	-9 ≤ h ≤ 9, -25 ≤ k ≤ 25, -11 ≤ l ≤ 10	-9 ≤ h ≤ 9, -25 ≤ k ≤ 25, -11 ≤ l ≤ 10
Reflections collected	29105	29029	29119	29209	29346
Independent reflections	2908 [R_{int} = 0.0148, R_{sigma} = 0.0278]	2891 [R_{int} = 0.0150, R_{sigma} = 0.0289]	2890 [R_{int} = 0.0152, R_{sigma} = 0.0287]	2881 [R_{int} = 0.0156, R_{sigma} = 0.0288]	2886 [R_{int} = 0.0158, R_{sigma} = 0.0295]
Data/restraints/parameters	2908/0/194	2891/0/194	2890/0/194	2881/0/194	2886/0/194
Goodness-of-fit on F^2	1.146	1.156	1.165	1.168	1.183
Final R indexes [I>=2σ (I)]	R_1 = 0.0509, wR_2 = 0.1320	R_1 = 0.0481, wR_2 = 0.1193	R_1 = 0.0473, wR_2 = 0.1118	R_1 = 0.0472, wR_2 = 0.1111	R_1 = 0.0485, wR_2 = 0.1194
Final R indexes [all data]	R_1 = 0.0524, wR_2 = 0.1332	R_1 = 0.0494, wR_2 = 0.1202	R_1 = 0.0487, wR_2 = 0.1128	R_1 = 0.0486, wR_2 = 0.1120	R_1 = 0.0496, wR_2 = 0.1202
Largest diff. peak/hole / e Å^{-3}	0.736/-0.661	0.675/-0.507	0.584/-0.543	0.713/-0.600	0.805/-0.427
Mosaicity	0.38	0.39	0.38	0.39	0.39
CCDC number	1947077	1947076	1947075	1947074	1947073

Identification code	**2_160K**	**2_140K**	**2_120K**	**2_100K**	**2_260K-R**
Empirical formula	$C_{32}H_{29}N_3O_9Zn_2$	$C_{32}H_{29}N_3O_9Zn_2$	$C_{32}H_{29}N_3O_9Zn_2$	$C_{32}H_{29}N_3O_9Zn_2$	$C_{32}H_{29}N_3O_9Zn_2$
Formula weight	730.32	730.32	730.32	730.32	730.32
Temperature/K	160(2)	140(2)	120(2)	100(2)	260-R(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/m$	$P2_1/m$	$P2_1/m$	$P2_1/m$	$P2_1/m$
a/Å	8.3338(2)	8.3268(3)	8.3037(4)	8.2872(3)	8.4179(3)
b/Å	21.5667(5)	21.5993(12)	21.5270(10)	21.5164(11)	21.5823(8)
c/Å	9.4299(2)	9.4395(9)	9.4220(4)	9.4099(4)	9.4363(3)
α/°	90	90	90	90	90
β/°	109.248(1)	109.159(1)	109.043(1)	109.039(1)	109.676(1)
γ/°	90	90	90	90	90
Volume/Å^3	1600.12(6)	1603.69(19))	1592.05(13)	1586.10(12)	1614.27(10)
Z	2	2	2	2	2
ρ_{calc}g/cm^3	1.516	1.512	1.523	1.529	1.503
μ/mm^{-1}	1.557	1.554	1.565	1.571	1.543
F(000)	748	748	748	748	748
Crystal size/mm^3	0.496 × 0.378 × 0.054	0.496 × 0.378 × 0.054	0.496 × 0.378 × 0.054	0.496 × 0.378 × 0.054	0.496 × 0.378 × 0.055
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
θ range for data collection/°	2.288 to 24.995	2.589 to 25.000	2.475 to 24.999	2.478 to 24.995	2.479 to 24.997
Index ranges	-9 ≤ h ≤ 9, -25 ≤ k ≤ 25, -11 ≤ l ≤ 10	-9 ≤ h ≤ 9, -25 ≤ k ≤ 25, -11 ≤ l ≤ 11	-9 ≤ h ≤ 9, -25 ≤ k ≤ 25, -11 ≤ l ≤ 11	-9 ≤ h ≤ 9, -25 ≤ k ≤ 25, -11 ≤ l ≤ 11	-10 ≤ h ≤ 10, -25 ≤ k ≤ 25, -10 ≤ l ≤ 11
Reflections collected	49288	58775	40167	24940	28954
Independent reflections	2887 [R_{int} = 0.0162, R_{sigma} = 0.0433]	2881 [R_{int} = 0.0139, R_{sigma} = 0.0405]	2863 [R_{int} = 0.1344, R_{sigma} = 0.0520]	2850 [R_{int} = 0.0451, R_{sigma} = 0.0446]	2899 [R_{int} = 0.0149, R_{sigma} = 0.0281]
Data/restraints/parameters	2887/0/194	2881/0/194	2863/0/194	2850/0/194	2899/0/194
Goodness-of-fit on F^2	1.108	1.188	1.029	1.181	1.161
Final R indexes [I>=2σ (I)]	R_1 = 0.0481, wR_2 = 0.1201	R_1 = 0.0490, wR_2 = 0.1135	R_1 = 0.0691, wR_2 = 0.1396	R_1 = 0.0646, wR_2 = 0.1412	R_1 = 0.0511, wR_2 = 0.1294
Final R indexes [all data]	R_1 = 0.0516, wR_2 = 0.1225	R_1 = 0.0545, wR_2 = 0.1201	R_1 = 0.1000, wR_2 = 0.1477	R_1 = 0.0777, wR_2 = 0.1474	R_1 = 0.0529, wR_2 = 0.1307
Largest diff. peak/hole / e Å^{-3}	0.915/-0.805	0.931/-0.864	0.788/-0.564	0.904/-1.007	0.657/-0.591
Mosaicity	0.39	0.38	0.38	0.39	0.38
CCDC number	1947072	1947071	1947070	1947069	1947078

Table S4. **Unit cell axes at variable temperatures for 2**.

T **(K)**	***a*** **(Å)**	**St. dev.***	***b*** **(Å)**	**St. dev.***	***c*** **(Å)**	**St. dev. ***
260	8.4208	0.0004	21.5873	0.0009	9.4367	0.0004
240	8.4039	0.0004	21.5861	0.0010	9.4367	0.0004
220	8.3866	0.0003	21.5858	0.0008	9.4357	0.0003
200	8.3674	0.0003	21.5772	0.0008	9.4332	0.0003
180	8.3498	0.0003	21.5720	0.0008	9.4328	0.0003
160	8.3338	0.0002	21.5667	0.0005	9.4299	0.0002
140	8.3268	0.0003	21.5993	0.0012	9.4395	0.0004
120	8.3037	0.0004	21.5270	0.0010	9.4220	0.0004
100	8.2872	0.0003	21.5164	0.0011	9.4099	0.0004
260-R	8.4179	0.0003	21.5823	0.0008	9.4363	0.0003

*Standard deviation calculated from unit cell refinement using the Apex III software suite.

Table S5. **Unit cell angles and volumes at variable temperatures for 2**.

T **(K)**	***β*** **(°)**	**St. dev. ***	**V(Å^3)**	**St. dev.***	**Crystal mosaicity**
260	109.674	0.001	1615.28	0.12	0.38
240	109.586	0.001	1612.84	0.13	0.39
220	109.511	0.001	1610.19	0.10	0.38
200	109.423	0.001	1606.19	0.10	0.39
180	109.338	0.001	1603.20	0.10	0.39
160	109.248	0.001	1600.12	0.06	0.39
140	109.159	0.001	1603.69	0.19	0.38
120	109.043	0.001	1592.05	0.13	0.38
100	109.039	0.001	1586.10	0.12	0.39
260-R	109.676	0.001	1614.27	0.10	0.38

*Standard deviation calculated from unit cell refinement using the Apex III software suite.

Table S6. List of selected C-H$\cdots\pi$ interactions in **1** in the temperature range 260 to 100 K.

Temperature (K)	**Donor(D)-H$\cdots$Acceptor(A)**	**H$\cdots$A distance (Å)**	**D$\cdots$A distance (Å)**	**D-H$\cdots$A angle (º)**
100	C10-H10$\cdots$*i*1	2.632(1)	3.499(1)	150.19(1)
	C21-H21$\cdots$*i*2	3.413(1)	4.092(1)	130.34(1)
	C4-H4$\cdots$*i*3	3.126(1)	4.004(1)	154.30(1)
120	C10-H10$\cdots$*i*1	2.642(1)	3.498(1)	150.13(2)
	C21-H21$\cdots$*i*2	3.401(1)	4.086(1)	130.89(2)
	C4-H4$\cdots$*i*3	3.140(1)	4.013(1)	153.53(2)
140	C10-H10$\cdots$*i*1	2.653(1)	3.510(1)	150.28(1)

	C21-H21···*i*2	3.389(1)	4.080(1)	131.42(1)
	C4-H4···*i*3	3.157(1)	4.025(1)	152.77(1)
160	C10-H10···*i*1	2.676(1)	3.531(1)	149.97(1)
	C21-H21···*i*2	3.371(1)	4.071(1)	132.25(1)
	C4-H4···*i*3	3.189(1)	4.047(1)	151.22(1)
180	C10-H10···*i*1	2.684(1)	3.539(1)	150.12(1)
	C21-H21···*i*2	3.368(1)	4.067(1)	132.16(1)
	C4-H4···*i*3	3.203(1)	4.058(1)	150.61(1)
200	C10-H10···*i*1	2.698(1)	3.552(1)	149.88(1)
	C21-H21···*i*2	3.358(1)	4.060(1)	132.48(1)
	C4-H4···*i*3	3.219(1)	4.073(1)	150.54(1)
220	C10-H10···*i*1	2.758(1)	3.563(1)	149.93(1)
	C21-H21···*i*2	3.359(1)	4.057(1)	132.74(1)
	C4-H4···*i*3	3.253(1)	4.091(1)	149.52(1)
240	C10-H10···*i*1	2.730(1)	3.575(1)	149.90(1)
	C21-H21···*i*2	3.343(1)	4.045(1)	133.13(1)
	C4-H4···*i*3	3.271(1)	4.106(1)	149.13(1)
260	C10-H10···*i*1	2.751(1)	3.586(1)	149.89(1)
	C21-H21···*i*2	3.352(1)	4.046(1)	133.21(1)
	C4-H4···*i*3	3.298(1)	4.121(1)	148.74(1)

*i*1 = centroid of C2-C7, *i*2 = centroid of C9-C13 and N1 and *i*3 = centroid of C17-C21 and N2
Standard deviations of non-bonding distances were calculated using Diamond version 4.4.1.[7]

Table S7. List of selected $\pi\cdots\pi$ interactions in **1** in the temperature range 260 to 100 K.

T(K)	*i*1··· *i*3 (Å)
100	4.114(1)
120	4.124(1)
140	4.139(1)
160	4.164(1)
180	4.168(1)
200	4.181(1)
220	4.192(1)
240	4.202(1)
260	4.211(1)

Standard deviations of non-bonding distances were calculated using Diamond version 4.4.1.[7]

Table S8. List of Zn··· Zn non-bonding distances across bpp ligands and N1···N2 non-bonding distances along the *a* axis in **1** in the temperature range 260 to 100 K.

T(K)	Zn1··· Zn1 (Å)	N1··· N2 (Å)
100	11.751(2)	8.612(1)
120	11.744(3)	8.606(2)
140	11.740(1)	8.604(1)
160	11.757(1)	8.617(1)
180	11.742(2)	8.610(1)
200	11.744(2)	8.613(1)
220	11.746(2)	8.613(1)
240	11.750(2)	8.619(1)
260	11.752(2)	8.617(1)

Standard deviations of non-bonding distances were calculated using Diamond version 4.4.1.[7]

Table S9. List of non-bonding distances and angles (Fig. 4, main text) involving tp linkages along the *c* axis in **1** in the temperature range 260 to 100 K.

T(K)	**d1 (Å)**	**d2 (Å)**	**θ_1 (°)**
100	10.828(1)	19.646(4)	130.221(1)
120	10.825(2)	19.645(5)	130.286(2)
140	10.823(3)	19.641(3)	130.291(1)
160	10.827(1)	19.641(2)	130.193(1)
180	10.823(1)	19.635(3)	130.221(1)
200	10.822(1)	19.629(3)	130.158(1)
220	10.821(1)	19.622(3)	130.098(1)
240	10.821(1)	19.617(3)	130.042(1)
260	10.820(1)	19.612(3)	130.000(1)

Standard deviations of non-bonding distances were calculated using Diamond version 4.4.1.[7]

Table S10. List of selected C-H···π interactions in **2** in the temperature range 260 to 100 K.

T (K)	C9···O2 (Å)	H9···O2 (Å)	∠C9-H9···O2 (°)	C7···O2 (Å)	H7···O2 (Å)	∠C7-H7···O2 (°)
100	3.160(6)	2.487(4)	127.8(1)	3.248(8)	2.549(5)	130.5(1)
120	3.169(6)	2.489(4)	128.4(1)	3.249(8)	2.554(5)	130.2(1)
140	3.176(4)	2.505(3)	127.7(1)	3.257(6)	2.559(3)	130.5(1)
160	3.176(3)	2.503(2)	127.8 (1)	3.253(4)	2.553(2)	130.7(1)
180	3.176(4)	2.504(2)	127.8(1)	3.258(6)	2.561(3)	130.3(1)
200	3.181(3)	2.506(2)	128.1(1)	3.259(4)	2.561(2)	130.5(1)
220	3.186(3)	2.516(2)	128.3(1)	3.266(4)	2.572(2)	130.9(1)
240	3.189(3)	2.519(2)	128.4(1)	3.269(4)	2.574(2)	131.0(1)
260	3.193(4)	2.528(3)	128.6(1)	3.264(6)	2.575(4)	131.3(1)

Standard deviations of non-bonding distances were calculated using Diamond version 4.4.1.[7]

Table S11. List of selected $\pi\cdots\pi$ interactions in **2** in the temperature range 260 to 100 K.

T (K)	$\pi\cdots\pi$ distance (*i*4–*i*5) (Å)	∠*i*4–*i*5–Zn1; θ_2 (°)
100	3.501(1)	104.96(2)
120	3.512(1)	104.92(2)
140	3.515(2)	105.18(1)
160	3.517(1)	105.23(1)
180	3.525(1)	105.29(1)
200	3.532(1)	105.32(1)
220	3.539(1)	105.35(1)
240	3.545(1)	105.40(1)
260	3.552(1)	105.44(1)

*i*4 = centroid of C6, C7, C8, C6*, C7* and C8*, *i*5 = centroid of N1, C9-C13
Standard deviations of non-bonding distances were calculated using Diamond version 4.4.1.[7]

Table S12. List of Zn···Zn non-bonding distances across the bpp ligand and N1···N2 non-bonding distances along the *b* axis in **2** in the temperature range 260 to 100 K.

T(K)	Zn1··· Zn1 (Å)	N1··· N2 (Å)
100	10.776(1)	8.413(6)
120	10.780(1)	8.421(6)
140	10.835(1)	8.464(5)
160	10.823(1)	8.446(3)
180	10.828(1)	8.444(4)
200	10.834(1)	8.448(3)
220	10.843(1)	8.452(3)
240	10.848(1)	8.448(3)
260	10.850(1)	8.449(4)

Standard deviations of non-bonding distances were calculated using Diamond version 4.4.1.[7]

Table S13. List of P···R and O···Q non-bonding distances in **2** (Fig. 7, main text) in the temperature range 260 to 100 K.

T(K)	*P*··· *R* (Å)	*O*··· *Q* (Å)
100	8.287(1)	17.919(1)
120	8.304(1)	17.942(1)
140	8.327(1)	17.960(2)
160	8.334(1)	17.930(1)
180	8.350(1)	17.925(1)
200	8.367(1)	17.915(1)
220	8.386(1)	17.909(1)
240	8.404(1)	17.902(1)
260	8.420(1)	17.891(1)

Standard deviations of non-bonding distances were calculated using Diamond version 4.4.1.[7]

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