Electronic Supplementary Material (ESI) for Chemical Communications
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Supplementary Information

Synthesis:

All starting materials were used without further purification as pursued by Sigma-Aldrich.

Synthesis of [$ZnBr_2$(2,2′-bipy)] (**1**): 4.5 mmol of zinc acetate (824 mg) were dissolved in 5 ml of H_2O. 1.1 ml of HBr 47.6 % (9 mmol) was added drop wise under stirring. This solution was added to a solution of 4.4 mmol of 2,2′-bipyridine in 20 ml of methanol and refluxed for 2 hours to allow the evaporation of acetic acid. The resulting white precipitate was filtrated in a sintered filter. 1mmol of the product (381 mg) was dissolved in 5 ml of DMSO. Large crystals were obtained over night by slow evaporation on an eating plate at 40 ˚C.

Thermal Analysis:

Differential scanning calorimetry (DSC) measurements were performed on TA DSC Q-2000 under nitrogen flux by cycling, between room temperature and -70 ˚C, 3 to 5 mg of coarsely ground crystalline **1**.

Variable temperature optical microscopy scans were conducted on an Olympus microscope equipped with a LINKAM cell.

Optical Microscopy:

A LINKAM LNP95 controller and a LINKAM THMS600-PS stage were used for variable temperature optical microscopy analysis, while images were recorded with a QIMAGING FAST 1394 QUICAM. Videos were edited with WINDOWS LIVE MOVIE MAKER software.

Crystallography:

Crystal structures at varied temperature were determined by X-ray diffraction on a Bruker APEX 2 DUO. The structures were solved and refined using the programs SHELXS-97 and SHELXL-97 (G. M. Sheldrick; *Acta Cryst.* 2008, A64, 112-122) respectively. The program X-Seed (L. J. Barbour; *J. Supr. Chem.* 2001, **1** (4–6), 189-191) was used as an interface to the SHELX programs, and to prepare the figures.

Crystal data for 1_273: $C_{10}H_8Br_2N_2Zn$, M = 381.37, colourless prism, 0.20 × 0.20 × 0.20 mm^3, monoclinic, space group $C2/c$ (No. 15), a = 10.7501(5), b = 14.7970(8), c = 7.7792(4) Å, β =

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97.911(3)°, V = 1225.65(11) Å^3, Z = 4, D_c = 2.067 g/cm^3, F_{000} = 728, MoKα radiation, λ = 0.71073 Å, T = 273(2)K, 2θ_{max} = 74.8º, 8487 reflections collected, 3167 unique (R_{int} = 0.0394). Final *GooF* = 0.944, *R1* = 0.0361, *wR2* = 0.0847, *R* indices based on 1614 reflections with I >2sigma(I) (refinement on F^2), 69 parameters, 0 restraints. Lp and absorption corrections applied, μ = 8.492 mm^{-1}.

Crystal data for 1_252: $C_{10}H_8Br_2N_2Zn$, M = 381.37, colourless prism, 0.20 × 0.20 × 0.20 mm^3, monoclinic, space group *C*2/*c* (No. 15), a = 10.7281(5), b = 14.8021(7), c = 7.7704(3) Å, β = 98.098(2)°, V = 1221.62(9) Å^3, Z = 4, D_c = 2.074 g/cm^3, F_{000} = 728, MoKα radiation, λ = 0.71073 Å, T = 252(2)K, 2θ_{max} = 75.8º, 8497 reflections collected, 3191 unique (R_{int} = 0.0378). Final *GooF* = 0.955, *R1* = 0.0364, *wR2* = 0.0829, *R* indices based on 1737 reflections with I >2sigma(I) (refinement on F^2), 69 parameters, 0 restraints. Lp and absorption corrections applied, μ = 8.520 mm^{-1}.

Crystal data for 1_232: $C_{10}H_8Br_2N_2Zn$, M = 381.37, colourless prism, 0.20 × 0.20 × 0.20 mm^3, monoclinic, space group *C*2/*c* (No. 15), a = 10.7106(3), b = 14.8067(5), c = 7.7624(3) Å, β = 98.299(2)°, V = 1218.14(7) Å^3, Z = 4, D_c = 2.080 g/cm^3, F_{000} = 728, MoKα radiation, λ = 0.71073 Å, T = 232(2)K, 2θ_{max} = 75.8º, 8472 reflections collected, 3184 unique (R_{int} = 0.0362). Final *GooF* = 1.014, *R1* = 0.0374, *wR2* = 0.0828, *R* indices based on 1866 reflections with I >2sigma(I) (refinement on F^2), 69 parameters, 0 restraints. Lp and absorption corrections applied, μ = 8.544 mm^{-1}.

Crystal data for 1_212: $C_{10}H_8Br_2N_2Zn$, M = 381.37, colourless prism, 0.20 × 0.20 × 0.20 mm^3, triclinic, space group *P*-1 (No. 2), a = 7.8238(11), b = 9.0676(12), c = 9.2577(14) Å, α = 113.055(7), β = 95.086(7), γ = 95.526(6)°, V = 595.75(15) Å^3, Z = 2, D_c = 2.126 g/cm^3, F_{000} = 364, MoKα radiation, λ = 0.71073 Å, T = 212(2)K, 2θ_{max} = 75.7º, 7863 reflections collected, 4566 unique (R_{int} = 0.1561). Final *GooF* = 1.085, *R1* = 0.1545, *wR2* = 0.4051, *R* indices based on 2501 reflections with I >2sigma(I) (refinement on F^2), 136 parameters, 0 restraints. Lp and absorption corrections applied, μ = 8.735 mm^{-1}.

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Crystal data for 1_191: $C_{10}H_8Br_2N_2Zn$, M = 381.37, colourless prism, 0.20 × 0.20 × 0.20 mm^3, triclinic, space group P-1 (No. 2), a = 7.8185(9), b = 9.0276(10), c = 9.2664(12) Å, α = 113.539(6), β = 95.267(6), γ = 95.631(5)°, V = 590.54(12) Å^3, Z = 2, D_c = 2.145 g/cm^3, F_{000} = 364, MoKα radiation, λ = 0.71073 Å, T = 191(2)K, $2\theta_{max}$ = 76.1°, 8008 reflections collected, 4698 unique (R_{int} = 0.1681). Final *GooF* = 1.589, *R1* = 0.1525, *wR2* = 0.4581, *R* indices based on 2633 reflections with I >2sigma(I) (refinement on F^2), 136 parameters, 0 restraints. Lp and absorption corrections applied, μ = 8.812 mm^{-1}.

Crystal data for 1_172: $C_{10}H_8Br_2N_2Zn$, M = 381.37, colourless prism, 0.20 × 0.20 × 0.20 mm^3, triclinic, space group P-1 (No. 2), a = 7.8183(10), b = 9.0188(12), c = 9.2659(14) Å, α = 113.807(7), β = 95.380(7), γ = 95.722(6)°, V = 588.30(14) Å^3, Z = 2, D_c = 2.153 g/cm^3, F_{000} = 364, MoKα radiation, λ = 0.71073 Å, T = 172(2)K, $2\theta_{max}$ = 75.0°, 7771 reflections collected, 4567 unique (R_{int} = 0.1637). Final *GooF* = 1.695, *R1* = 0.1618, *wR2* = 0.4651, *R* indices based on 2713 reflections with I >2sigma(I) (refinement on F^2), 136 parameters, 0 restraints. Lp and absorption corrections applied, μ = 8.846 mm^{-1}.

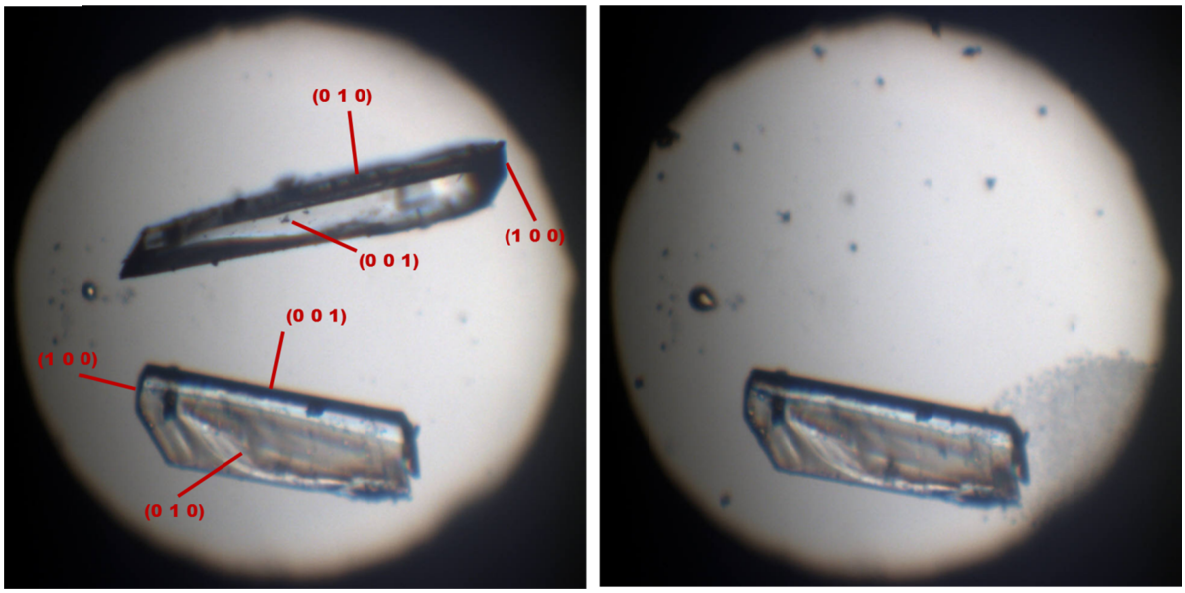

Figure S1: Crystals of 1 as seen on an optical microscope during the variable temperature experiment. The principal crystal faces are indicated,

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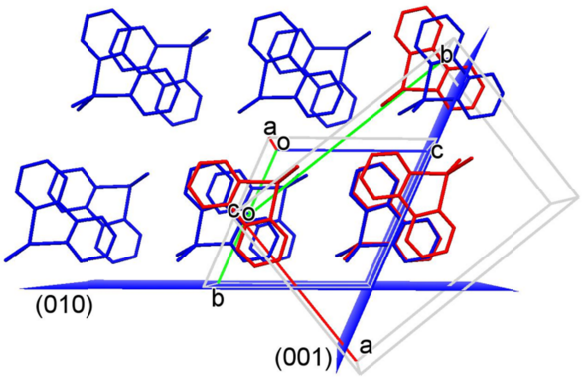

Figure S2: Crystal structure of 1HT (red) and 1LT (blue) viewed alond the c and a axis respectively. The monoclinic and triclinic unit cells, as well as the (0 0 1) and (0 1 0) planes relative to the triclinic form, are shown.

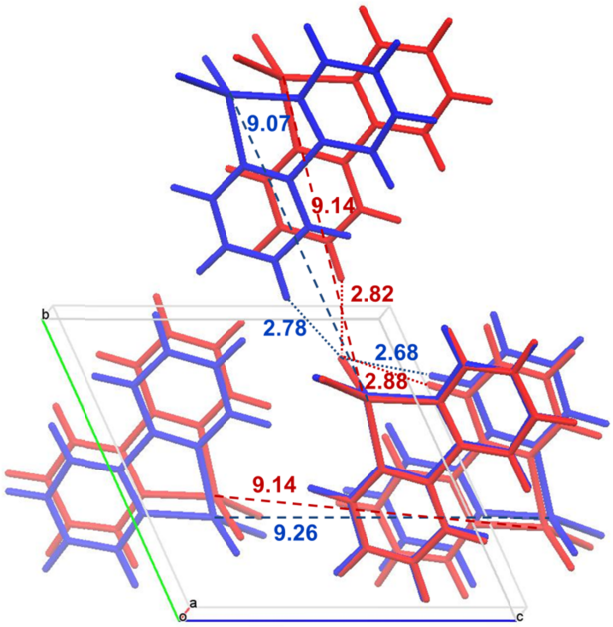

Figure S3: Comparison of **1HT** (red) and **1LT** (blue) measured at 232 and 212 K respectively. The distance between metal centers along the reduced cell axes and the shortest Br···H contacts are reported in Å; distances are calculated for neutron normalized C-H distances.

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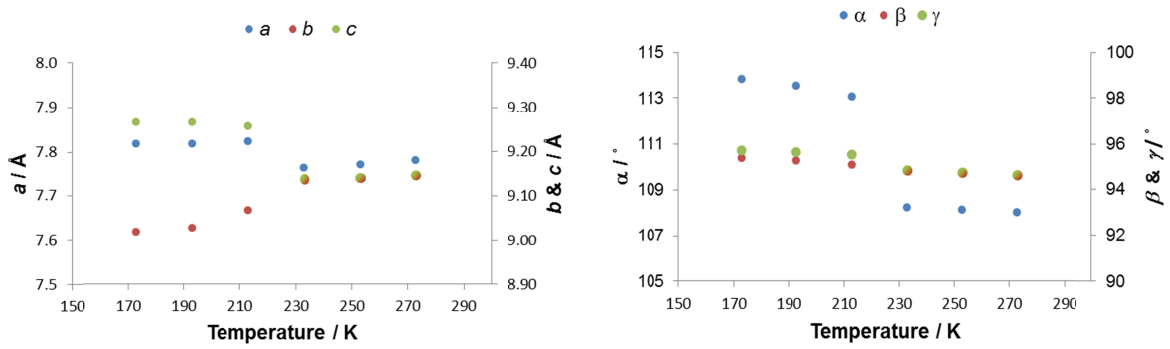

Figure S4: Cell metrix as function of temperature for **1**: axes (left) and angles (right).

Table S1. Linear thermal expansion coefficients along the reduced cell axes.

Delta T	α_a	α_b	α_c
172 - 191	1.28 x 10^6	48.79 x 10^6	2.70 x 10^6
191 - 212	33.89 x 10^6	221.54 x 10^6	-46.94 x 10^6
212 - 232	-392.39 x 10^6	383.89 x 10^6	-650.70 x 10^6
232 -252	51.53 x 10^6	17.89 x 10^6	17.89 x 10^6
252 - 273	56.63 x 10^6	24.07 x 10^6	24.07 x 10^6

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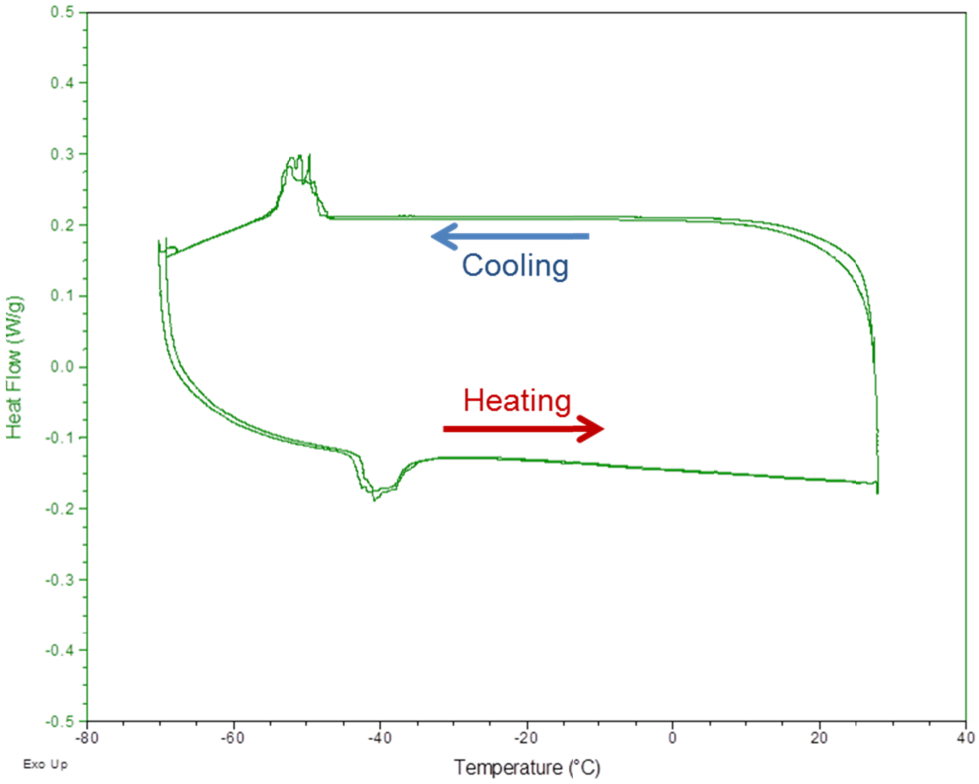

Figure S5: DSC analysis for **1.** Two successive cooling/heating cycles are shown.