Supplementary Information

Synthesis:
All starting materials were used without further purification as pursued by Sigma-Aldrich.
Synthesis of $[\text{ZnBr}_2(2,2'\text{-bipy})]$ (1): 4.5 mmol of zinc acetate (824 mg) were dissolved in 5 ml of H$_2$O. 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$_8$Br$_2$N$_2$Zn, $M = 381.37$, 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, $β =$
97.911(3)°, V = 1225.65(11) Å³, Z = 4, Dc = 2.067 g/cm³, F₀₀₀ = 728, MoKα radiation, λ = 0.71073 Å, T = 273(2)K, 2θmax = 74.8°, 8487 reflections collected, 3167 unique (Rint = 0.0394). Final GooF = 0.944, R1 = 0.0361, wR2 = 0.0847, R indices based on 1614 reflections with I >2σ(I) (refinement on F²), 69 parameters, 0 restraints. Lp and absorption corrections applied, μ = 8.492 mm⁻¹.

Crystal data for 1_252: C₁₀H₈Br₂N₂Zn, M = 381.37, colourless prism, 0.20 × 0.20 × 0.20 mm³, monoclinic, space group C2/c (No. 15), a = 10.7281(5), b = 14.8021(7), c = 7.7704(3) Å, β = 98.098(2)°, V = 1221.62(9) Å³, Z = 4, Dc = 2.074 g/cm³, F₀₀₀ = 728, MoKα radiation, λ = 0.71073 Å, T = 252(2)K, 2θmax = 75.8°, 8497 reflections collected, 3191 unique (Rint = 0.0378). Final GooF = 0.955, R1 = 0.0364, wR2 = 0.0829, R indices based on 1737 reflections with I >2σ(I) (refinement on F²), 69 parameters, 0 restraints. Lp and absorption corrections applied, μ = 8.520 mm⁻¹.

Crystal data for 1_232: C₁₀H₈Br₂N₂Zn, M = 381.37, colourless prism, 0.20 × 0.20 × 0.20 mm³, monoclinic, space group C2/c (No. 15), a = 10.7106(3), b = 14.8067(5), c = 7.7624(3) Å, β = 98.299(2)°, V = 1221.62(9) Å³, Z = 4, Dc = 2.074 g/cm³, F₀₀₀ = 728, MoKα radiation, λ = 0.71073 Å, T = 232(2)K, 2θmax = 75.8°, 8497 reflections collected, 3191 unique (Rint = 0.0378). Final GooF = 0.955, R1 = 0.0364, wR2 = 0.0829, R indices based on 1737 reflections with I >2σ(I) (refinement on F²), 69 parameters, 0 restraints. Lp and absorption corrections applied, μ = 8.520 mm⁻¹.

Crystal data for 1_212: C₁₀H₈Br₂N₂Zn, M = 381.37, colourless prism, 0.20 × 0.20 × 0.20 mm³, 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) Å³, Z = 2, Dc = 2.126 g/cm³, F₀₀₀ = 364, MoKα radiation, λ = 0.71073 Å, T = 212(2)K, 2θmax = 75.7°, 7863 reflections collected, 4566 unique (Rint = 0.1561). Final GooF = 1.014, R1 = 0.1545, wR2 = 0.4051, R indices based on 2501 reflections with I >2σ(I) (refinement on F²), 136 parameters, 0 restraints. Lp and absorption corrections applied, μ = 8.735 mm⁻¹.
Crystal data for 1_191: C\textsubscript{10}H\textsubscript{8}Br\textsubscript{2}N\textsubscript{2}Zn, \( M = 381.37 \), colourless prism, 0.20 \( \times \) 0.20 \( \times \) 0.20 mm\(^3\), triclinic, space group \( P-1 \) (No. 2), \( a = 7.8185(9) \), \( b = 9.0276(10) \), \( c = 9.2664(12) \) Å, \( \alpha = 113.539(6) \), \( \beta = 95.267(6) \), \( \gamma = 95.631(5) \)°, \( V = 590.54(12) \) Å\(^3\), \( Z = 2 \), \( D_c = 2.145 \) g/cm\(^3\), \( F_{000} = 364 \), MoK\( \alpha \) radiation, \( \lambda = 0.71073 \) Å, \( T = 191(2) \)K, \( 2\theta_{\text{max}} = 76.1 \)°, 8008 reflections collected, 4698 unique (\( R_{\text{int}} = 0.1681 \)). Final \( \text{Goof} = 1.589 \), \( R1 = 0.1525 \), \( wR2 = 0.4581 \), \( R \) indices based on 2633 reflections with \( I > 2 \sigma(I) \) (refinement on \( F^2 \)), 136 parameters, 0 restraints. \( \mu \) and absorption corrections applied, \( \mu = 8.812 \) mm\(^{-1}\).

Crystal data for 1_172: C\textsubscript{10}H\textsubscript{8}Br\textsubscript{2}N\textsubscript{2}Zn, \( M = 381.37 \), colourless prism, 0.20 \( \times \) 0.20 \( \times \) 0.20 mm\(^3\), triclinic, space group \( P-1 \) (No. 2), \( a = 7.8183(10) \), \( b = 9.0188(12) \), \( c = 9.2659(14) \) Å, \( \alpha = 113.807(7) \), \( \beta = 95.380(7) \), \( \gamma = 95.722(6) \)°, \( V = 588.30(14) \) Å\(^3\), \( Z = 2 \), \( D_c = 2.153 \) g/cm\(^3\), \( F_{000} = 364 \), MoK\( \alpha \) radiation, \( \lambda = 0.71073 \) Å, \( T = 172(2) \)K, \( 2\theta_{\text{max}} = 75.0 \)°, 7771 reflections collected, 4567 unique (\( R_{\text{int}} = 0.1637 \)). Final \( \text{Goof} = 1.695 \), \( R1 = 0.1618 \), \( wR2 = 0.4651 \), \( R \) indices based on 2713 reflections with \( I > 2 \sigma(I) \) (refinement on \( F^2 \)), 136 parameters, 0 restraints. \( \mu \) and absorption corrections applied, \( \mu = 8.846 \) mm\(^{-1}\).

**Figure S1:** Crystals of 1 as seen on an optical microscope during the variable temperature experiment. The principal crystal faces are indicated,
**Figure S2:** Crystal structure of 1HT (red) and 1LT (blue) viewed along 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.
Figure S4: Cell matrix as function of temperature for 1: axes (left) and angles (right).

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

<table>
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<th>Delta T</th>
<th>$\alpha_a$</th>
<th>$\alpha_b$</th>
<th>$\alpha_c$</th>
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<td>172 - 191</td>
<td>$1.28 \times 10^6$</td>
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<td>$2.70 \times 10^5$</td>
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<tr>
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<td>$33.89 \times 10^5$</td>
<td>$221.54 \times 10^5$</td>
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<td>$383.89 \times 10^5$</td>
<td>$-650.70 \times 10^5$</td>
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<td>$17.89 \times 10^5$</td>
<td>$17.89 \times 10^5$</td>
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<tr>
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<td>$24.07 \times 10^5$</td>
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Figure S5: DSC analysis for 1. Two successive cooling/heating cycles are shown.