Supplementary Information

Temperature-dependent guest reorientation: a reversible order-disorder transformation in a single crystal.

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Single crystal X-ray diffraction:
X-ray diffraction data were collected for the same single crystal at 100, 173 243 and 313 K on a Bruker Apex-II Duo diffractometer employing Mo *K*α radiation. The structures was solved and refined using the programs SHELXS-97 and SHELXL-97 respectively. The program X-Seed was used as an interface to the SHELX programs, and to prepare the figures. The atoms of the meta-xylene were refined isotropically

Crystal data for $\mathbf{1_{100}}$: $C_{62}H_{56}N_6NiS_2$, M = 1007.95, lilac plate, 0.300 × 0.200 × 0.050 mm^3, monoclinic, space group $P2_1/n$ (No. 14), a = 10.4770(4), b = 23.0584(10), c = 22.7761(9) Å, β = 99.028(2)°, V = 5434.1(4) Å^3, Z = 4, D_c = 1.232 g/cm^3, F_{000} = 2120, MoKα radiation, λ = 0.71073 Å, T = 100(2)K, $2\theta_{max}$ = 60.9º, 53528 reflections collected, 14861 unique (R_{int} = 0.0537). Final *GooF* = 1.030, *R1* = 0.0466, *wR2* = 0.1020, *R* indices based on 10178 reflections with I > 2(I) (refinement on F^2), 644 parameters, 0 restraints. Lp and absorption corrections applied, μ = 0.478 mm^{-1}.

Crystal data for $\mathbf{1_{173}}$: $C_{62}H_{56}N_6NiS_2$, M = 1007.96, lilac plate, 0.30 × 0.20 × 0.05 mm^3, monoclinic, space group $P2_1/n$ (No. 14), a = 10.4770(4), b = 23.0584(10), c = 22.7761(9) Å, β = 99.028(2)°, V = 5434.2(4) Å^3, Z = 4, D_c = 1.232 g/cm^3, F_{000} = 2120, MoKα radiation, λ = 0.71073 Å, T = 173(2)K, $2\theta_{max}$ = 61.0º, 54274 reflections collected, 15062 unique (R_{int} = 0.0731). Final *GooF* = 0.965, *R1* = 0.0572, *wR2* = 0.1402, *R* indices based on 8786 reflections with I >2sigma(I) (refinement on F^2), 622 parameters, 1 restraint. Lp and absorption corrections applied, μ = 0.478 mm^{-1}.

Crystal data for $\mathbf{1_{243}}$: $C_{62}H_{56}N_6NiS_2$, M = 1007.96, lilac plate, 0.30 × 0.25 × 0.05 mm^3, monoclinic, space group $C2/c$ (No. 15), a = 10.5793(2), b = 23.1141(4), c = 22.8660(4) Å, β = 99.5160(10)°, V = 5514.50(17) Å^3, Z = 4, D_c = 1.214 g/cm^3, F_{000} = 2120, MoKα radiation, λ = 0.71073 Å, T = 243(2)K, $2\theta_{max}$ = 60.9º, 27586 reflections collected, 7636 unique (R_{int} = 0.1401). Final *GooF* = 0.852, *R1* = 0.0609, *wR2* = 0.1583, *R* indices based on 4045 reflections with I >2sigma(I) (refinement on F^2), 323 parameters, 1 restraint. Lp and absorption corrections applied, μ = 0.471 mm^{-1}.

Crystal data for $\mathbf{1}_{\mathbf{313}}$: $C_{62}H_{56}N_6NiS_2$, M = 1007.96, lilac plate, 0.30 × 0.25 × 0.05 mm^3, monoclinic, space group $C2/c$ (No. 15), a = 10.6221(7), b = 23.1917(16), c = 23.0275(15) Å, β = 99.649(4)°, V = 5592.4(6) $Å^3$, Z = 4, D_c = 1.197 g/cm^3, F_{000} = 2120, MoKα radiation, λ = 0.71073 Å, T = 313(2)K, $2\theta_{max}$ = 60.9º, 27880 reflections collected, 7766 unique (R_{int} = 0.0451). Final *GooF* = 0.989, *R1* = 0.0602, *wR2* = 0.1739, *R* indices based on 3833 reflections with I >2sigma(I) (refinement on F^2), 305 parameters, 1 restraint. Lp and absorption corrections applied, μ = 0.465 mm^{-1}.

Powder X-ray diffraction:
X-ray powder diffraction patterns were collected at room temperature on a PANalytical X'Celerator diffractometer employing Cu $K\alpha_{1,2}$ radiation.

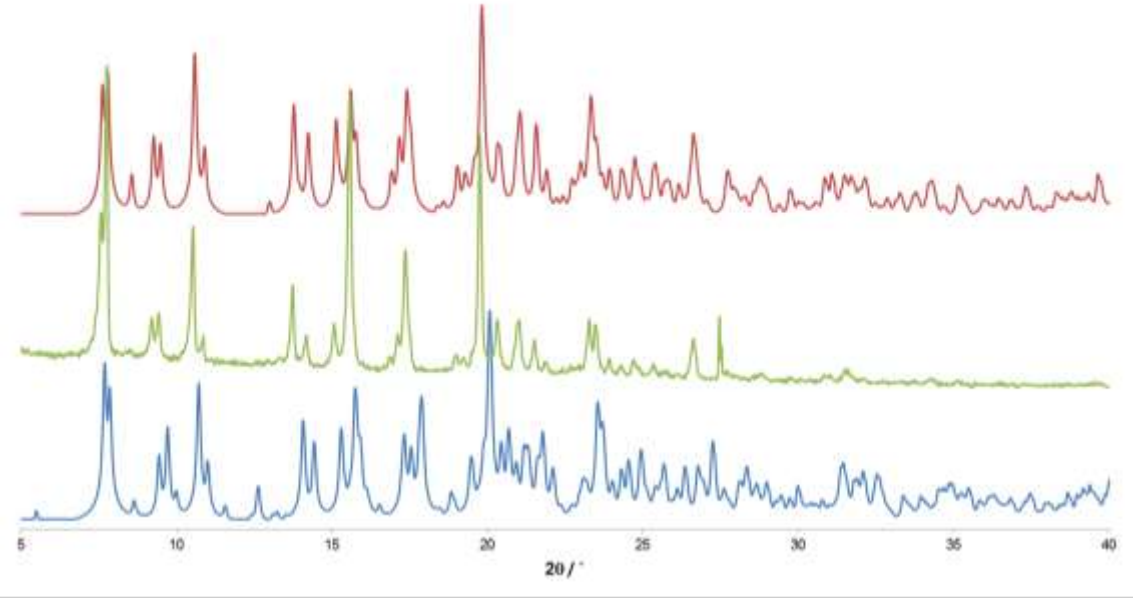

Figure S1. Comparison of powder X-ray diffraction measured for **1** (middle) with the patterns simulated* for the structure determined at 100 K (bottom) and at 313 K (top).
* experimental Cu $Ka_{1,2}$ diffraction patterns were simulated from the crystallographic information file using a step size of 0.02˚ and a Gaussian peak shape with full width at maximum height (FWMH) of 0.1 in 2θ.

Thermal Analysis:
TA Instruments Q100 DSC and Q500 TGA were used for thermal analyses. Samples with a mass of 3 to 5 mg were measured under nitrogen at a heating/cooling rate of 15 °C per minute. TA UNIVERSAL ANALYSIS software was used for data graphics and data analysis.

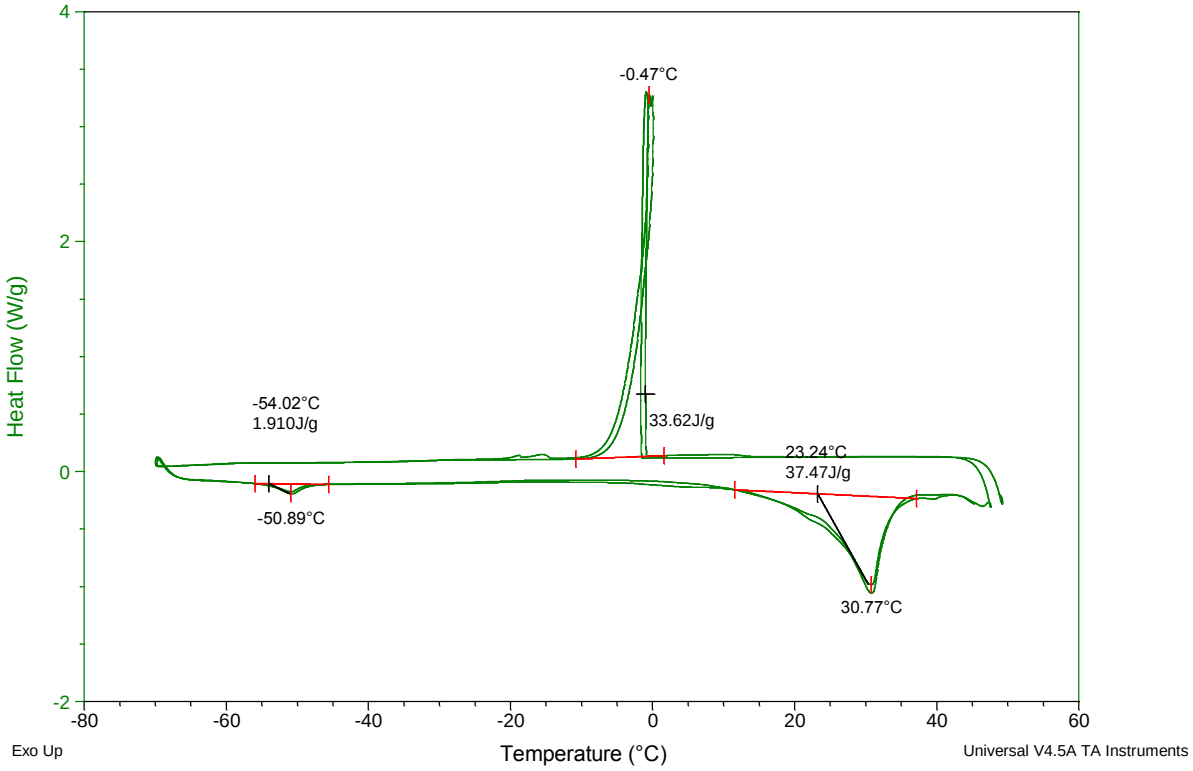

Figure S2. Two consecutive DSC cycles for **1** show the reversibility of the phase transitions.

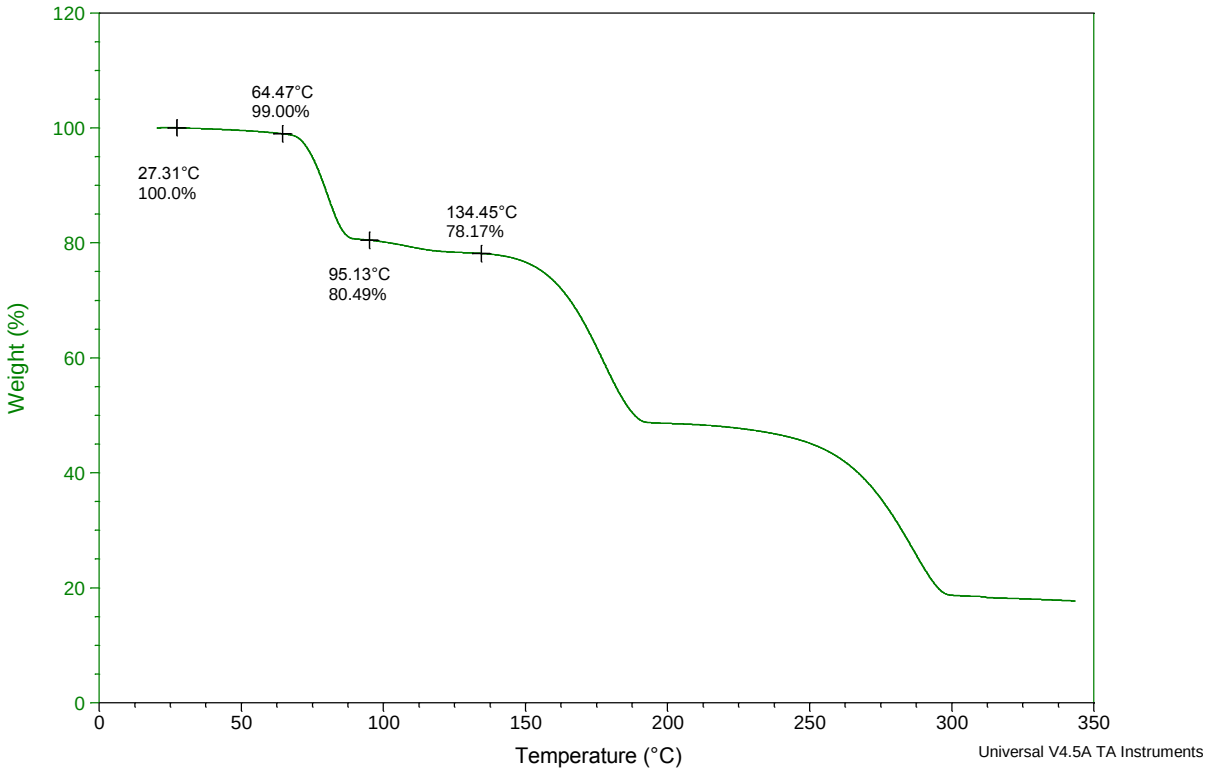

Figure S3. TGA for **1**: shows a loss of about 20% between 65 and 95 ˚C and a smaller loss of about 2% 95 and 130 ˚C.