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Electronic Supplementary Information

Temperature-Directed Structural Recurrence in Low-Symmetric Co(II) Complexes and Nanocrystals

*Yan-Yan Yin, Xiao-Yan Chen, Xiao-Chang Cao, Wei Shi, Peng Cheng**

Department of Chemistry and Key Laboratory of Advanced Energy Materials Chemistry (MOE), Nankai University, Tianjin 300071, P. R. China

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Synthesis:

1. Instrument: All reagents and solvents employed were commercially available and used as received without further purification. Infrared spectra were obtained from KBr pellets on a Bio-Rad FTS 135 Plus spectrometer in the 400-4000 cm^{-1} region. Elemental analyses for C, H and N were carried out by using a Perkin–Elmer analyzer. Thermal analyses (under oxygenated atmosphere, heating rate of 10 °C min^{-1}) were carried out in a Labsys NETZSCH TG 209 Setaram apparatus. Single X-ray diffraction data were collected on a Rigaku Saturn 007 CCD diffractometer with graphite-monochromatized Mo-Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods using SHELXS-97 and refined by least-squares procedures on F_o^2 with SHELXL-97 by minimizing the function $\sum\omega(F_o^2 - F_c^2)^2$, where F_o and F_c are, respectively, the observed and calculated structure factors. The hydrogen atoms were located geometrically and refined isotropically. Powder X-ray diffraction data were collected by using a D/Max-2500 X-ray diffractometer with Cu Kα radiation. The morphologies of the samples were inspected using field emission scanning electron microscope (SEM, Hitachi S-3500N) and Transmission electron microscopy (TEM, FEI Tecnai 20) operated at 200 kV. CD experiments were performed on a Jasco J-715 spectropolarimeter at room temperature. The temperature-dependent ac dielectric permittivity measurements were performed with an impedance analyzer Agilent 4294A. The dielectric hysteresis loop of polarization was measured on a single crystal sample using a Precision Premier II ferroelectric tester (Radiant) under an ac field of a triangular waveform.

2. Synthesis of bulk crystals of 1 and 2: In a typical experiment, an aqueous solution of $Co(CH_3COO)_2{\cdot}4H_2O$ (5.0 mL, 0.5 mmol) was added to thiazolidine 2,4-dicaboxylic acid (0.5 mmol) in 10.0 mL water. The solution was mixed under vigorous stirring for 2 hours and then filtered. The filtrate was divided into three portions which were allowed to stand at certain temperatures (refrigerator (278 K); room temperature (298 K) and oven (353 K)). Salmon pink needle-like crystals were obtained after several days at 298 K (**1**). Yield: 24% based on cobalt salt. Elemental analysis (%) calcd for **1** ($C_5H_{11}O_7SNCo$): C, 20.57; H, 3.31; N, 5.13. Found: C, 20.84; H, 3.85; N, 4.86. IR (KBr, cm^{-1}): 3415, 3287, 1619, 1559, 1428, 1384, 1278-524; Purplish red needle-like crystals were obtained after several days at 278 K and 353 K with 38% and 41% yields, respectively. Elemental analysis (%) calcd for **2** ($C_5H_8O_{5.5}SNCo$): C, 23.47; H, 3.21; N, 4.99. Found **2** (crystallized at 278 K): C, 22.83; H, 3.31; N, 5.89; (crystallized at 353 K): C, 23.00; H, 3.09; N, 5.36. IR (KBr, cm^{-1}): 3415, 3287, 1619, 1559, 1428, 1384, 1278-524.

3. Synthesis of nanoscale products of N278, N298 and N353: $Co(CH_3COO)_2{\cdot}4H_2O$ (0.50 g, 2.0 mmol) was dissolved in water (40.0 mL) and added to a mixture of polyvinylpyrrolidone (PVP) aqueous solution (11.2 g, 140.0 mL). After a

few minutes of stirring, the aqueous solution of thiazolidine 2,4-dicaboxylic acid (0.34 g, 2.0 mmol, 20.0 mL) was added to this solution. The obtained solution was mixed under vigorous stirring for 2 hours at room temperature. Afterwards, it was left overnight at certain temperatures (278 K, 298 K, and 353 K, respectively). The mixtures were precipitated with 200.0 mL acetone to yield white suspension, isolated by centrifugation at 4000 rpm for 15 min. After removal of the supernatant, the particles were washed with ethanol (100.0 mL) several times. The ethanol suspension was centrifuged again for 15 min at 4000 rpm, and pink powders (**N278**, **N298** and **N353**) were obtained, respectively.

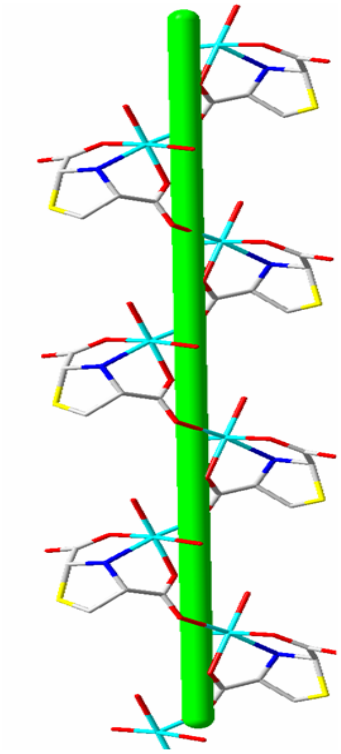

Fig. S1 The left handed chain of $\{[Co(\mu_2\text{-}L)(H_2O)_2]\cdot H_2O\}_n$ (**1**). The pitch of the helix is 9.63 Å, containing two Co(II) ions per turn. The color code: Co (cyan), N (blue), C (gray), S (yellow), O (red).

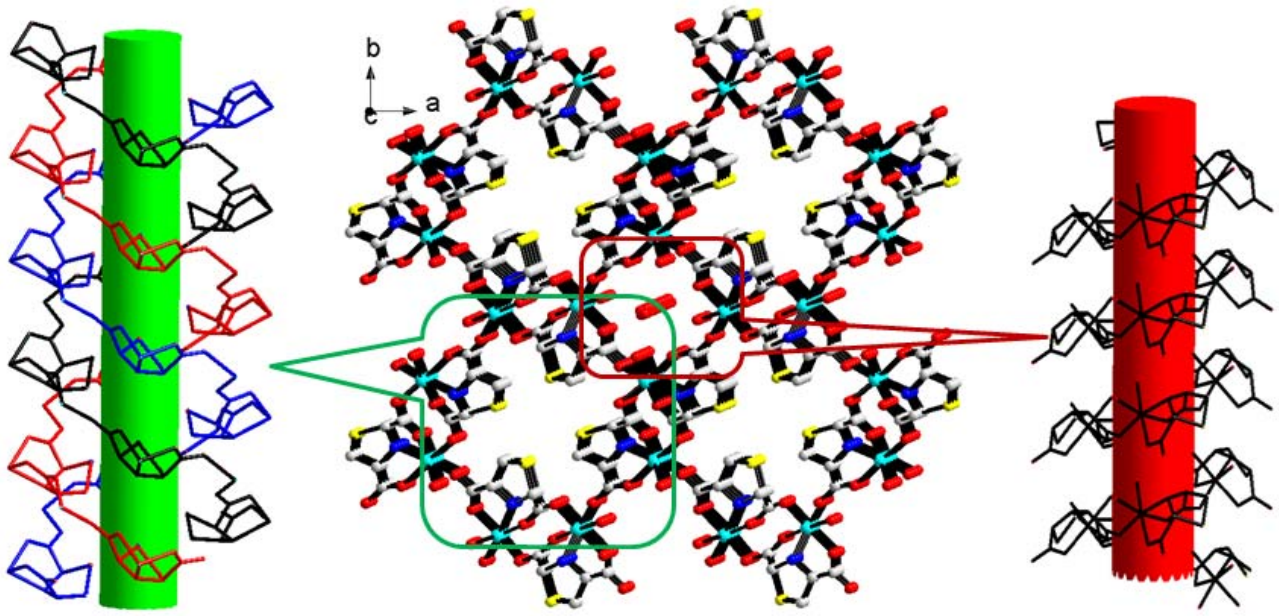

Fig. S2 Two kinds of channels in $\{[Co(\mu_3\text{-L})(H_2O)]\cdot 0.5H_2O\}_n$ (**2**). 1) Triple intertwist alternating left-handed helices forming a 1D hydrophobic channel with the distance from the cube center to the closest cobalt atom of 6.40 Å (green). 2) Linked by O3-C-O4 of the ligand, Co(II) ions are arranged in single right-handed helical chains which form a 1D hydrophilic open channel (red) which filled with lattice water. The pitch of the helix is 5.29 Å, containing four Co(II) ions per turn.

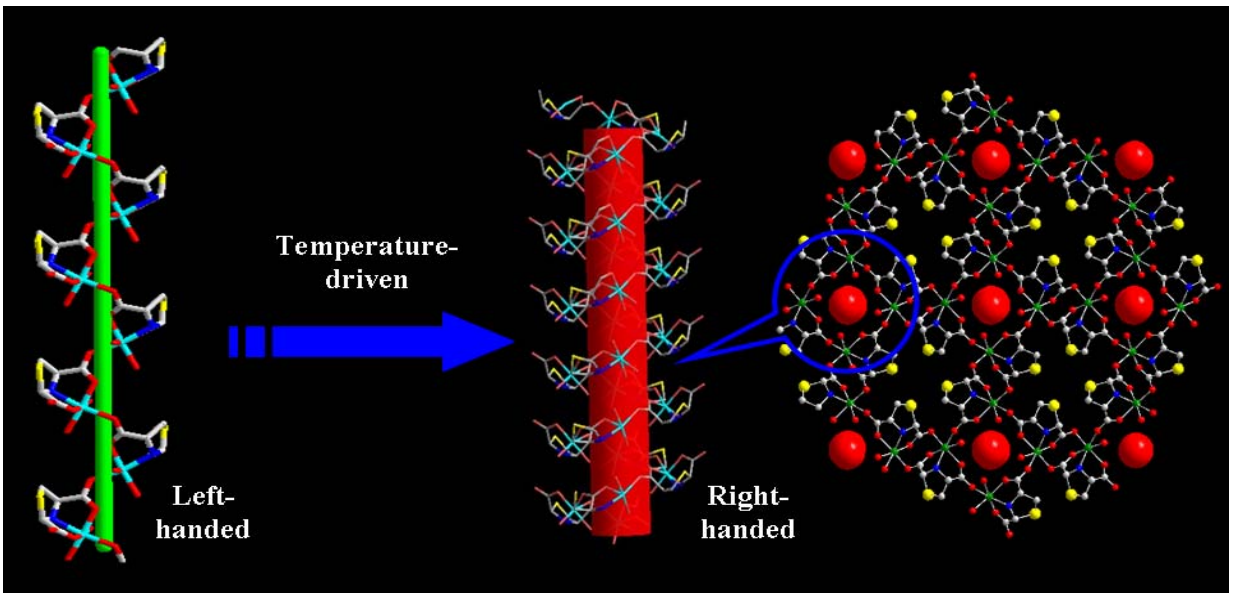

Fig. S3 Conformation conversion of helical chain {-Co-O3-C-O4-Co-}$_n$ via temperature adjustment. The color code: Co (cyan), N (blue), C (gray), S (yellow), O (red).

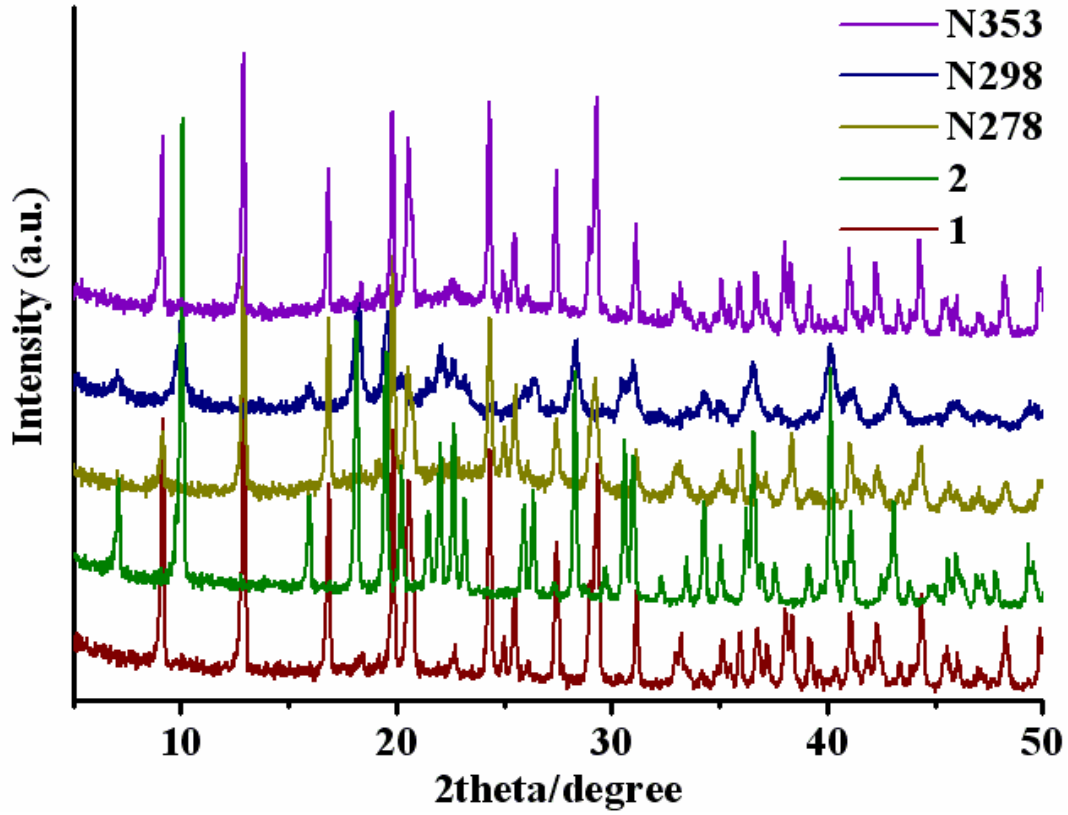

Fig. S4 PXRD patterns of **N278**, **N298** and **N353** as well as bulk complexes **1** and **2**.

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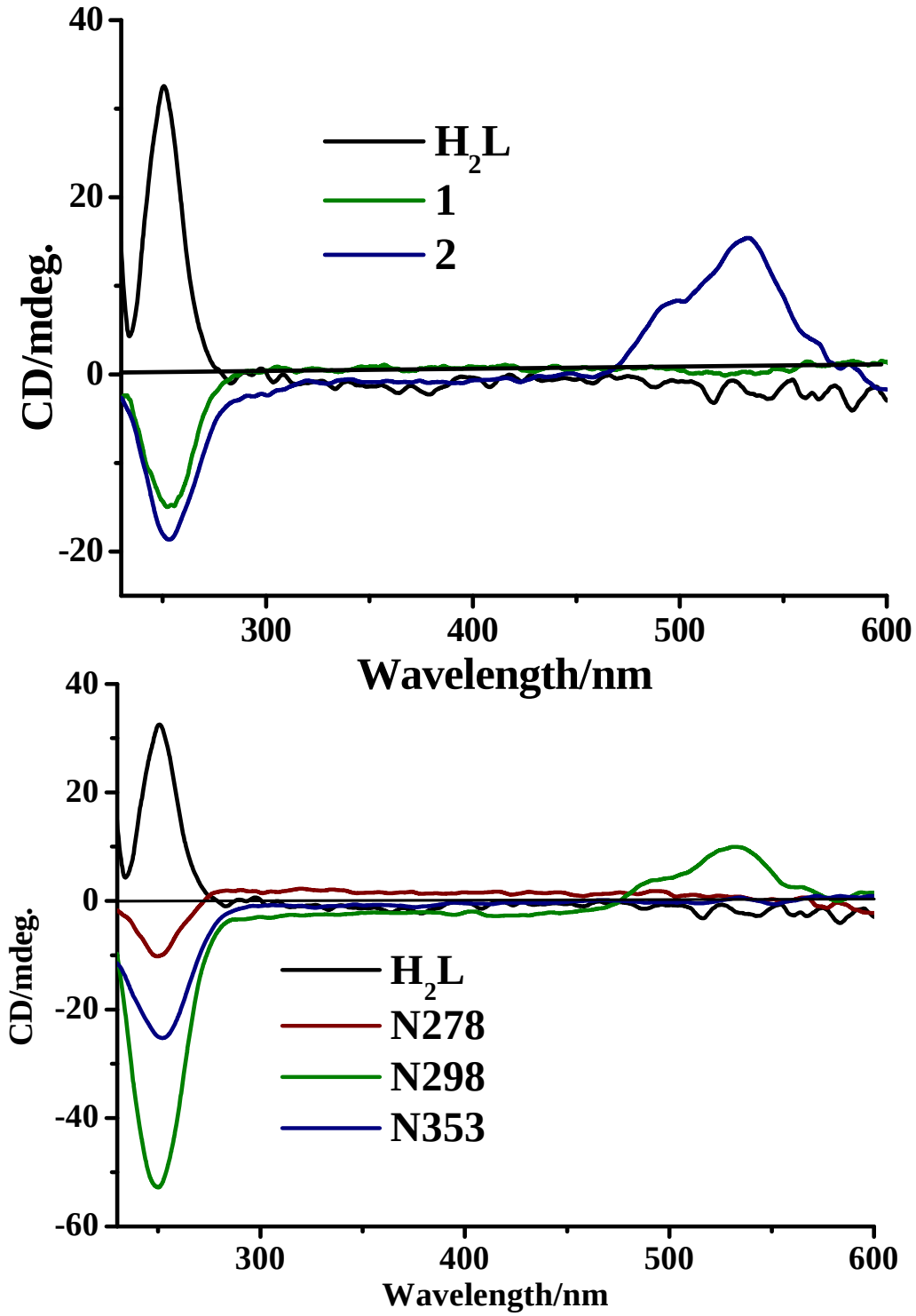

Fig. S5 CD patterns of the bulk- (up) and nano-crystals (bottom). The black lines are CD patterns of the free ligands.

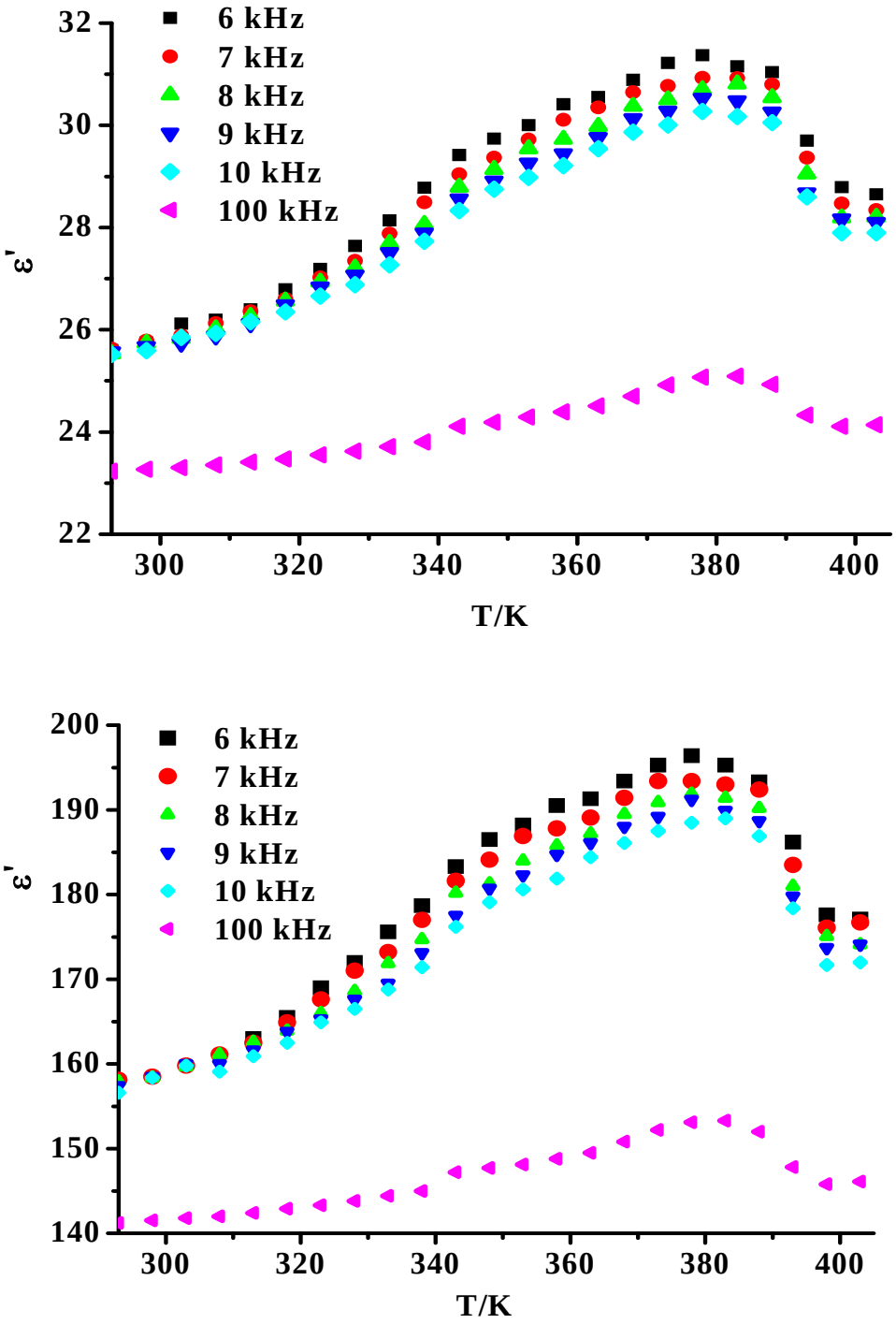

Fig. S6 Temperature dependencies of the real part of the permittivity of **1** (up) and **2** (bottom) at 6–100 kHz.

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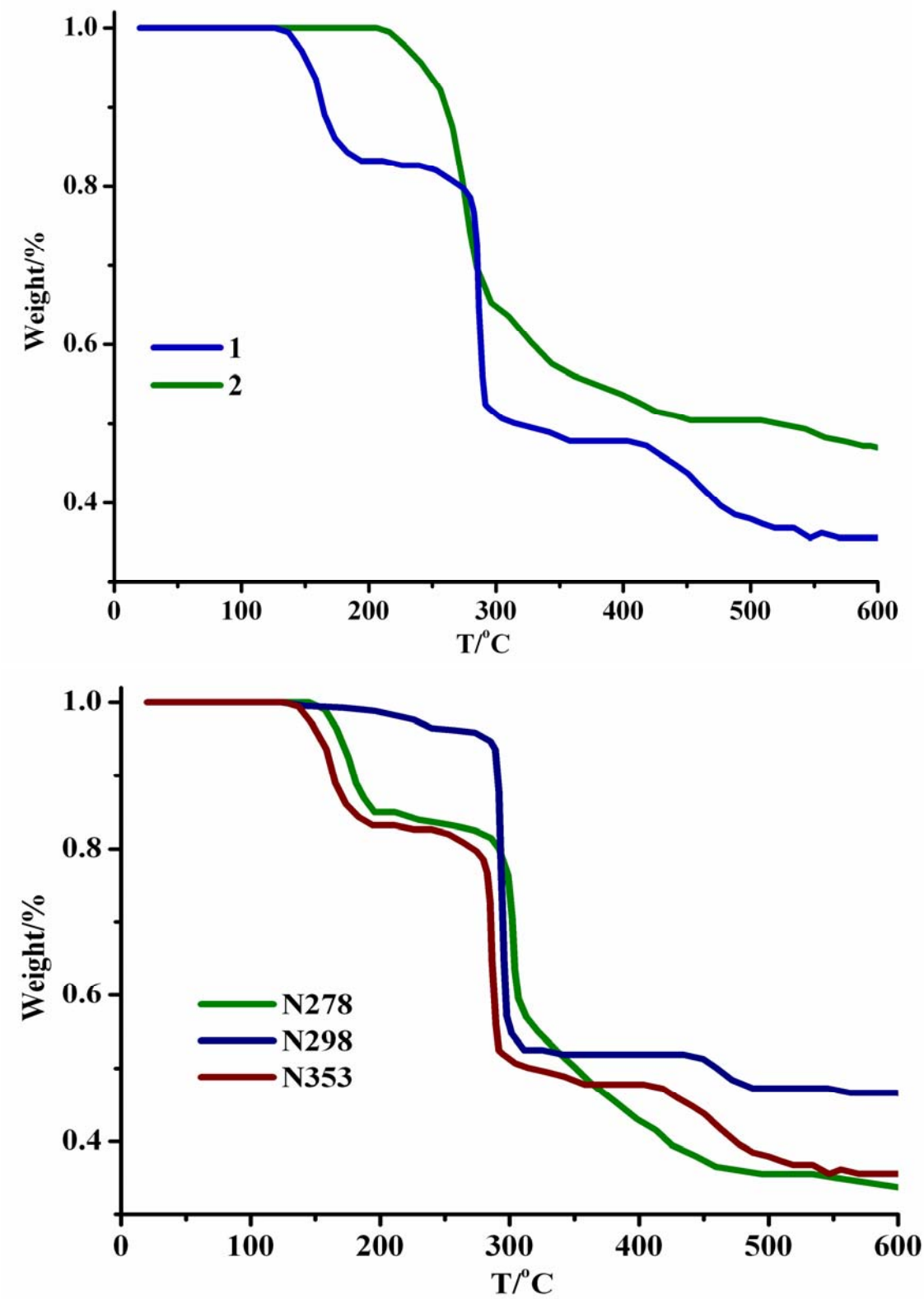

Fig. S7 Thermogravimetric analyses (TGA) of bulk crystals (up) and corresponding nanocrystals (bottom).

Table S1. Crystal data and structure refinements of **1** and **2**.

Compounds	**2** (crystallized at 278 K)	**1**	**2** (crystallized at 353 K)
Formula	$C_5H_8CoNO_{5.5}S$	$C_5H_{11}CoNO_7S$	$C_5H_8CoNO_{5.5}S$
Fw.	261.11	288.14	261.11
T (K)	293(2)	293(2)	293(2)
Crystal system	tetragonal	monoclinic	tetragonal
Space group	$P4_1$	$P2_1$	$P4_1$
a (Å)	12.3667(3)	5.3211(11)	12.2640(17)
b (Å)	12.3667(3)	9.6312(19)	12.2640(17)
c (Å)	5.2934(11)	9.764(2)	5.2535(11)
β (deg)	90	101.10(3)	90
V ($Å^3$)	809.6(3)	491.03(17)	790.2(2)
Z	4	2	4
ρ (mg/cm^3)	2.142	1.949	2.195
μ (mm^{-1})	2.373	1.977	2.431
F(000)	528	294	528
θ (deg)	3.29 to 27.46	3.90 to 27.47	3.32 to 24.46
Index ranges	-16≤h≤16	-6≤h≤6	-15≤h≤15
	-16≤k≤15	-12≤k≤12	-14≤k≤15
	-6≤l≤6	-12≤l≤12	-6≤l≤5
Flack parameter	0.03(5)	0.02(2)	0.01(3)
Max. and min. transmission	0.7973 and 0.5362	0.9805and 0.9076	0.7931 and 0.5291
GOF on F^2	1.108	1.075	1.102
R_1, R_2 [I > 2σ (I)]	0.0840, 0.1141	0.0401, 0.0743	0.0618, 0.0853
R_1, R_2 (all data)	0.1170, 0.1227	0.0476, 0.0763	0.0811, 0.0896
Largest diff. peak and hole ($e.Å^{-3}$)	0.880 and -0.499	0.393 and -0.469	0.454 and -0.526

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Table S2. Selected bond lengths (Å) and angles (deg) of **1** and **2**.

Compounds	**2** (crystallized at 278 K)	**1**	**2** (crystallized at 353 K)
Co(1)-O(1)#2	2.077(5)	—	2.053(4)
Co(1)-O(2)	2.041(6)	2.036(2)	2.040(4)
Co(1)-O(3)	2.080(5)	2.103(3)	2.071(4)
Co(1)-O(4)#1	2.118(6)	2.110(3)	2.093(5)
Co(1)-N(1)	2.147(6)	2.125(3)	2.133(5)
Co(1)-O(5)	2.076(6)	2.110(3)	2.072(4)
Co(1)-O(6)	—	2.065(3)	—
O(3)-C(4)	1.262(10)	1.250(4)	1.241(7)
O(4)-C(4)	1.276 (8)	1.260(4)	1.261(6)
N(1)-Co(1)-O(2)	81.3(2)	82.11(12)	81.24(19)
N(1)-Co(1)-O(3)	78.6(2)	78.52(11)	78.52(17)
O(2)-Co(1)-O(3)	93.8(2)	91.25(13)	93.48(17)
O(3)-Co(1)-O(4)#1	92.9(2)	92.02(10)	93.20(17)
O(3)-C(4)-C(3)	119.4(7)	119.6(3)	119.95(5)
O(3)-C(4)-O(4)	121.8(8)	123.9(3)	121.9(6)
C(4) -O(4)-Co(1)	133.1(6)	127.7(2)	134.4(5)

Symmetry transformations used to generate equivalent atoms: #1 -x,-y+1,z+1/2; #2 y,-x+1,z-1/4.