Electronic Supplementary Information

Tuning size and magnetic thermal hysteresis in new near room temperature spin crossover compound

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Synthesis of the ligand

The ligand 2-hydroxy-3-methyl-N'-((pyridin-2-yl)-ethylidene)benzohydrazide (**HL**) was prepared using similar method described in the literature.[1] Yield: 80 %. FT-IR (cm^{-1}): 3007(b), 2917, 2858, 1638, 1610, 1585, 1498, 1482, 1429, 1307, 1292, 1252, 1015, 1129, 831, 791, 640. Anal. Calcd for $C_{15}H_{15}N_3O_2$ (M = 269.30): C, 66.90; H, 5.61; N, 15.60. Found: C, 66.67; H, 5.68; N, 15.55 %.

Synthesis of the compound $Fe(AP\text{-}Mesal)_2$

The methanol solution (5 mL) of the ligand (54 mg, 0.2 mmol) with equimolar NaOH (7 mg, 0.2 mmol) and iron(II) perchlorate (75 mg, 0.2 mmol) in methanol solution (5 mL) were placed separately in the side arms of H-shaped tube, and the two solutions were carefully linked by methanol (5 mL) to allow slow liquid-to-liquid diffusion. Dark green crystals were formed in several weeks, which were not air sensitive and can be handled under a normal atmosphere.

Preparation of micro and nanoparticles

Sample 1. 1 mL of PEG-400 is added to a solution of $Fe(ClO_4)_2 \cdot 6H_2O$ (75 mg, 0.2 mmol) in 17 mL of water with a trace amount of ascorbic acid. AP-Mesal (80 mg, 0.3 mmol) is dissolved in 13 mL of methanol, adding 1 mL of PEG-400. After several minutes of stirring separately, the previous solution is added dropwise to the second solution forming a black-green solution. The mixture is stirred for 5 h and then filtered, washed with ethanol and water, dried in the atmosphere to yield **1**.

Sample 2. The same procedure as in sample **1** is used in this case, but $Fe(ClO_4)_2 \cdot 6H_2O$ was dissolved in 7 mL of water and AP-Mesal was dissolved in 13 mL of methanol.

Sample 3. The same procedure as in sample **1** is used in this case, but $Fe(ClO_4)_2 \cdot 6H_2O$ was

dissolved in 10 mL of water, AP-Mesal was dissolved in 20 mL of methanol, using 0.5 mL of PEG-400 in each solution.

Sample 4. The same procedure as in sample **1** is used in this case, but $Fe(ClO_4)_2 \cdot 6H_2O$ was dissolved in 10 mL of water.

Sample 5. The same procedure as in sample **3** is used in this case, but 1 mL of PEG-400 was added to each solution respectively.

Sample 6. The same procedure as in sample **3** is used in this case, but 5 mL of PEG-400 was added to each solution respectively.

Magnetic measurements

The variable temperature magnetic susceptibility measurements were carried out on sample constituted of monocrystals (~ 10 mg) using a Quantum Design MPMS-XL5 SQUID-Magnetometer at two field strengths (2 kOe and 5 kOe) in the heating an cooling mode within a temperature range from 2 to 390 K. Gelatine capsules were used as sample containers for measurements. The data were corrected for the magnetization of the sample holder, and diamagnetic corrections were estimated using Pascal's constants.[2]

The photomagnetic measurements were performed using a LD Pumped All-Solid-State Laser with 532 nm wavelength coupled *via* an optical fiber to the cavity of a Quantum Design MPMS-XL5 SQUID-Magnetometer operating with an external magnetic field of 10 kOe. The sample was located at the center of the standard sample holder produced by Quantum Design Company. The weight was estimated by comparing the thermal SCO curve with that for an accurately weighted sample. Standardized method for determining LIESST properties was followed.[3] After being cooled slowly to 10 K, the sample was irradiated and the change in magnetism followed. When the saturation point had been reached, the irradiation was ceased and the temperature increased at a rate of 0.3 K min^{-1} while the magnetization was measured every 1 K. T(LIESST) was determined from the minimum of the $d\chi_M T/dT$ vs. T curve. The data were corrected for the magnetization of the sample holder and the diamagnetic contributions, estimated from the Pascal's constants.

Physical characterization

Elemental analyses of carbon, hydrogen, and nitrogen were carried out with an Elementar Vario EL analyzer. Micro-IR spectroscopy studies were performed on a Nicolet Magna-IR 750 spectrophotometer in the 4000-650 cm^{-1} region (w, weak; b, broad; m, medium; s, strong). Powder X-ray diffraction (XRD) measurements were performed on a Bruker D8 Advance Diffraction diffractometer in the 2θ range from 5° to 60°, with Cu Kα radiation (λ= 0.15405 nm) at 40 Kv, 40 mA. The morphology and size of the samples were observed by SEM (LEO1530VP). Transmission electron microscopy (TEM) images were recorded using a Hitachi H-600 with an accelerating voltage of 100 kV. Thermal analyses were performed on SDT Q600 thermal analyzer (thermogravimetric analysis/differential thermal analysis, TGA/DTA) and Netzsch STA 449C TG-DSC thermoanalysis coupled with QMS403C quadrupole mass spectrometer in the range of 28℃-600℃ at heating rate of 10℃/min in air. DSC analyses were carried on Q100 differential scanning calorimeter (DSC) and Netzsch DSC 200 F3, under a nitrogen gas flow (50 mL min^{-1}) with a constant heating or cooling rate of 5 K min^{-1}. Temperature and enthalpy were calibrated using the melting point of indium.

References

1. P. V. Bernhardt, P. Chin, P. C. Sharpe and D. R. Richardson, *Dalton Trans.*, 2007, 3232.

2. L. N. Mulay and E. A. Boudreaux, *Theory and Applications of Molecular Diamagnetism*, John Wiley & Sons Inc., New York, 1976.

3. J.-F. Létard, P. Guionneau, O. Nguyen, J. S. Costa, S. Marcen, G. Chastanet, M. Marchivie and L. Goux-Capes, *Chem.-Eur. J.*, 2005, **11**, 4582; J.-F. Létard, *J. Mater. Chem.*, 2006, **16**, 2550; J.-F. Létard, C. Carbonera, E. Courcot and J. S. Costa, *Bull. Mater. Sci.*, 2006, **29**, 567.

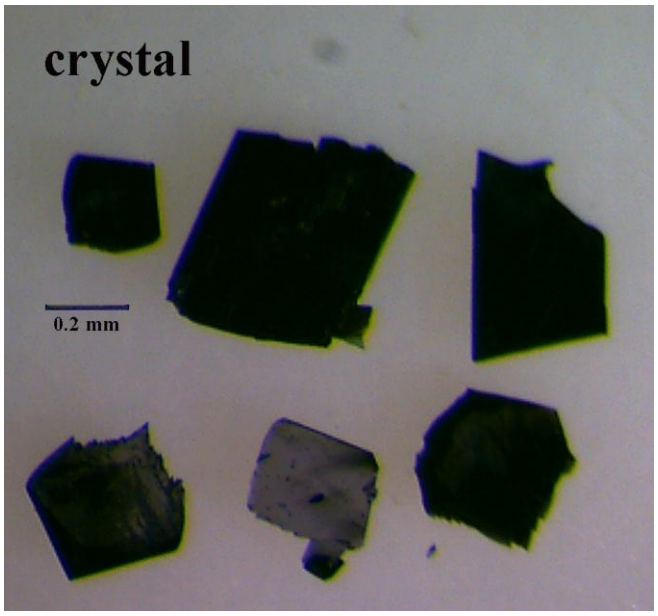


Figure S1. Microscope image of the crystals of Fe(AP-Mesal)$_2$.

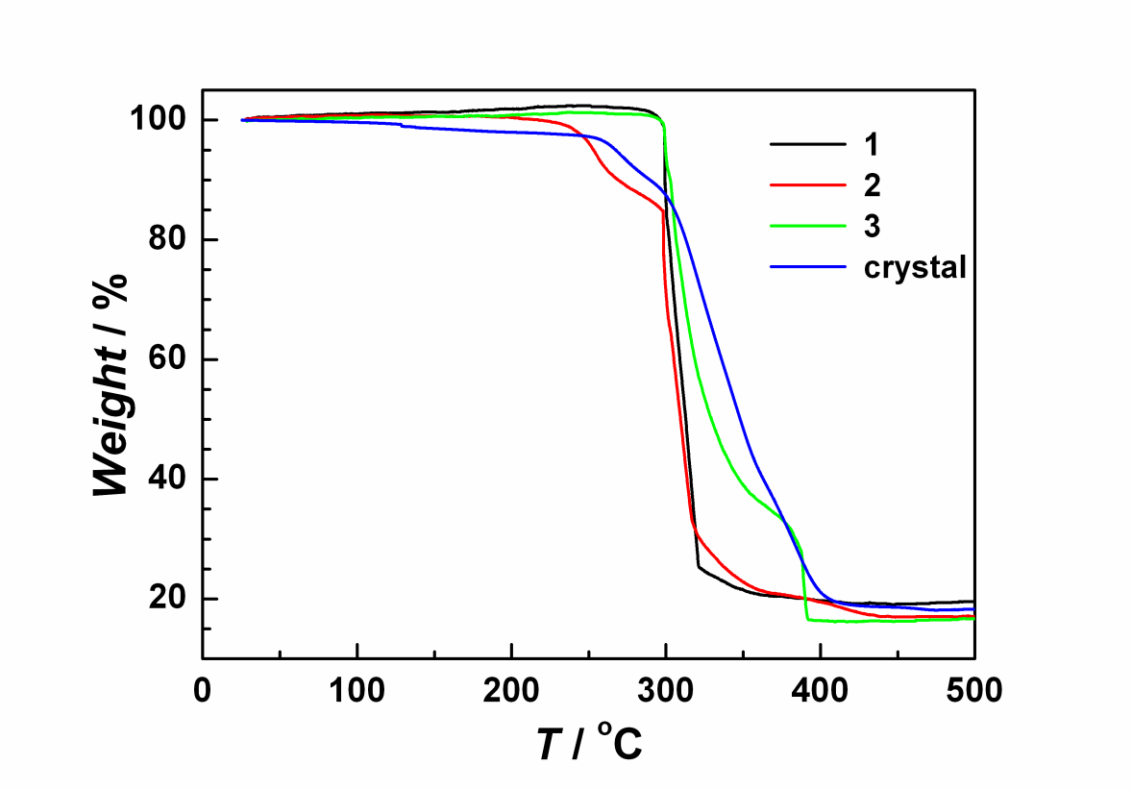
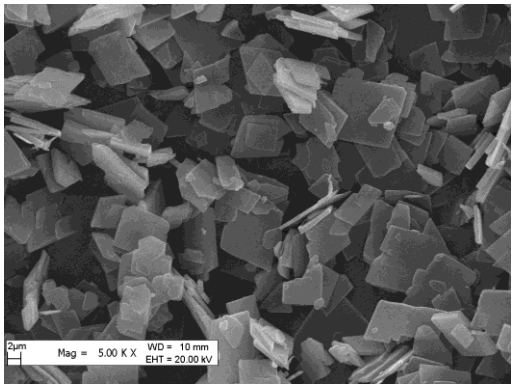
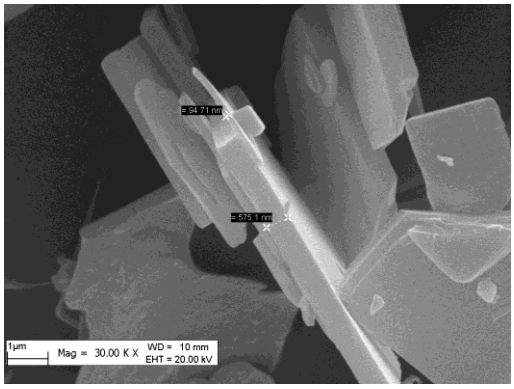


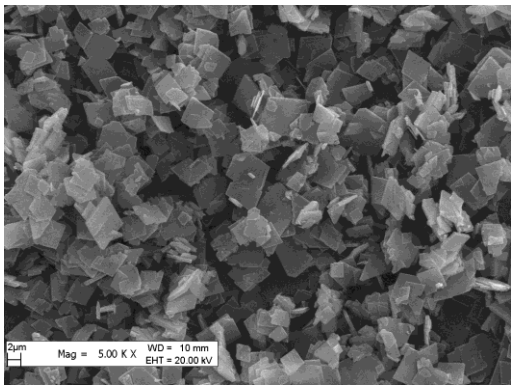
Figure S2. Thermal analysis of bulk crystals, sample **1**, sample **2** and sample **3**.



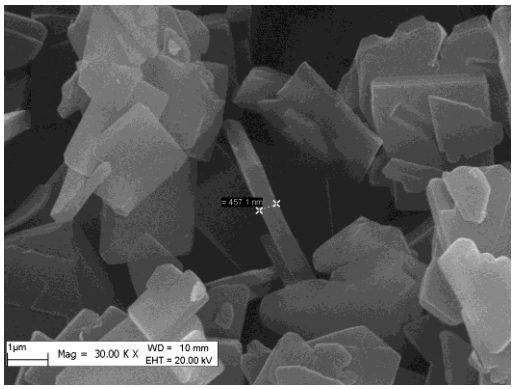
(a)



(b)



(c)



(d)

Figure S3. SEM images of sample **1** (a,b) and sample **2** (c,d).

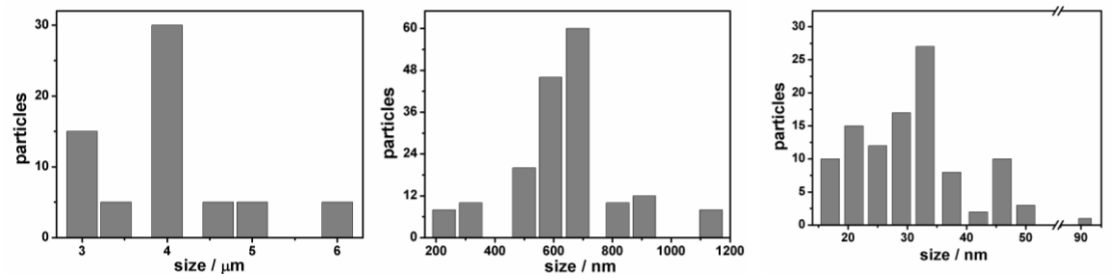


Figure S4. Size distribution histograms of sample **1** (left), **2** (middle) and **3** (right).

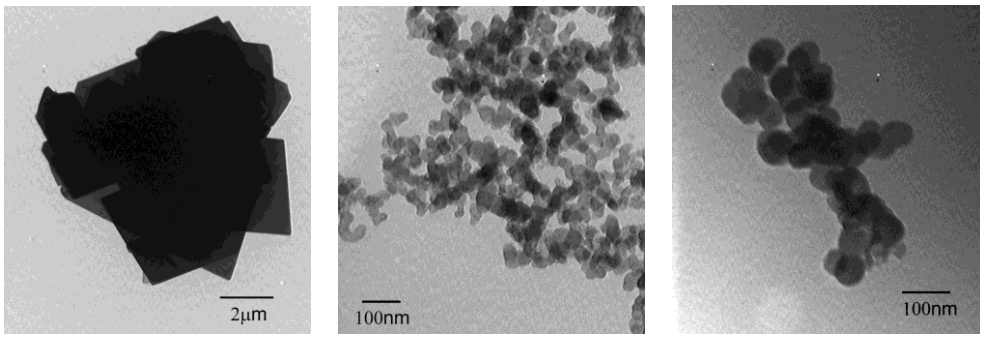


Figure S5. TEM images of sample **4** (left), **5** (middle) and **6** (right).

Table S1 Thermodynamic parameters of crystal and sample **1**-**3**.

compound	$T_{1/2}\uparrow$ (K)	$T_{1/2}\downarrow$ (K)	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
crystal	285	285	5.46	19.16
1	286	282	9.50	33.46
2	288	282	2.51	8.82
3	289	279	9.55	33.74