Electronic Supplementary Information

Facile Preparation of Hybrid Thin Films Composed of Spin-Crossover Nanoparticles and Carbon Nanotubes for Electrical Memory Devices

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Experimental details

General Information

All chemicals and solvents were of reagent grade and used without further purification. Si substrates were purchased from Matsuzaki Seisakusyo Co. LTD. UV-Visible absorption spectra were recorded with a Shimadzu UV-3150 double-beam spectrophotometer equipped with a temperature controller. The suspension of **1** was stirred during UV-vis absorption measurements to make the suspension homogeneous. Before the absorption spectra measurements, the temperature was maintained at a constant value for at least 5 minutes to stabilize the temperature. The magnetic susceptibility measurements were carried out on a Quantum Design MPMS-XL7AC superconducting quantum interference device (SQUID) magnetometer. The magnetic susceptibility was measured every 2 K, and measurements were made after waiting for stabilization at each temperature. The magnetic susceptibility at each temperature was measured 5 times, and the average value was used. The differential scanning calorimetry (DSC) measurements were carried out on a Perkin–Elmer DSC Diamond instrument under nitrogen atmosphere with 5 K min^{-1} scan rate. Field-emission scanning electron microscopy (FE-SEM) images of the films on silicon substrates were recorded using a JEOL JSM-7600F microscope, operating at 2 kV in JEOL gentle beam mode. Spin-coating was performed using MIKASA MS-A100 spin-coater. Sonication of the SWCNTs was carried out using an ultrasonic bath, Yamato1510 (BRANSON, Inc.).

Synthesis of $[Fe(Htrz)_2(trz)](BF_4)$ nanoparticles (1)

$[Fe(Htrz)_2(trz)](BF_4)$ nanoparticles were prepared according to literature procedure reported by Coronado.[1] The suspension of the nanoparticles in *n*-octane was then washed with ethanol as shown below.

A solution of $Fe(BF_4)_2{\cdot}6H_2O$ (0.5 g, 1.5 mmol) in water (3 mL) was added to a suspension of sodium dioctyl sulfosuccinate sodium salt (AOT, 5.0 g, 11.3 mmol) and behenic acid (1.0 g, 2.9 mmol) in *n*-octane (50 mL). A solution of 1,2,4-1*H*-triazole (Htrz, 0.31 g, 4.4 mmol) in ethanol (1.5 mL) was added to a solution of AOT (5 g, 11.3 mmol) in *n*-octane (50 mL). After stirring for several minutes at room temperature, the Htrz solution was added to the solution of $Fe(BF_4)_2{\cdot}6H_2O$. The mixture was stirred for 4 h at room temperature in air, resulting in a purple suspension. The obtained suspension was then centrifuged (3,000 rpm for 15 min) to yield a clear purple supernatant. The nanoparticles in the suspension were isolated by centrifugation (20,000 rpm for 2 h) and the obtained precipitate was dispersed again in 80 mL of ethanol. The ethanol suspension was centrifuged (20,000 rpm for 2 h) and the purple precipitate was collected. This ethanol washing process was carried out three times. The resultant precipitate, wet with ethanol,

was dispersed in various solvents. The precipitate was dried in vacuo for 12 h and aa dark purple solid was obtained, suitable for SQUID, DSC, and impedance spectroscopy measurements.
Anal. Calcd for $[Fe(Htrz)_2(trz)](BF_4)$ $(AOT)_{0.05}(H_2O)_{0.65}$, $(C_7H_{11.15}BF_4FeN_9Na_{0.05}OS_{0.05})$: C, 21.96; H, 2.94; B, 2.82; F, 19.85; Fe, 14.59; N, 32.93; Na, 0.30; O, 4.18; S, 0.42. Found: C, 21.93; H, 2.73; N, 32.95.

Preparation of thin films of 1

An ethanol solution of the nanoparticles having an absorbance of 1 for the *d–d* transition at 530 nm was prepared. The solution was filtered through 200 nm syringe filters and then used for coating. Si(100) substrates were rinsed with water, acetone, and ethanol. The substrates were then placed on the spin coater, covered by the nanoparticle solution, and then accelerated within 5 s to 1500 rpm for 30 s, resulting in thin films of **1**.

Preparation of composite films of 1 and single-walled carbon nanotube (SWCNT)

SWCNTs (HiPco Purified, NanoIntegris, 2.4 mg) were suspended in 20 mL of *o*-dichlorobenzene, and the suspension was sonicated for 100 h using water-bath sonication. The SWCNT suspension (5 mL) was then mixed with 10 mL of the ethanol solution of **1**, which had an absorbance of 2 at 530 nm. The mixture was gently stirred and used for film preparation. Si(100) substrates were rinsed with water, acetone, and ethanol. For spin coating, the substrates were placed on the spin coater, covered by the nanoparticle solution and then accelerated within 5 s to 1500 rpm for 30 s, resulting in the composite films of **1** and SWCNT.

Synchrotron X-ray diffraction experiments

Measurements were performed with a four-circle diffractometer having ϕ, χ, θ, and 2θ circles at beamline BL13XU for surface and interface structures, SPring-8 (λ = 1.006 Å). The φ, χ, and θ angles are for orienting a sample, and 2θ is for orienting the X-ray detector. Measurements were performed under helium gas. Each data set was recorded using a scintillation counter. The in-plane measurements were carried out at $\alpha = 0.1°$, where α is the X-ray incident angle to the sample surface. A solar slit (0.4°) was placed between the sample and the detector.

Measurements of impedance spectra

The impedance spectra of **1** in pellet form were measured from 313 K to 403 K using an impedance and gain-phase analyzer (Solartron SI 1260). The impedance cell was filled with dry N_2 at atmospheric pressure. A pressed powder pellet of **1** was sandwiched by two gold-coated electrodes with a 5 mm diameter and a 0.9 mm thickness. The measurements were performed at thermal equilibrium by holding for 30 min at each measuring temperature. ZView software was used to fit the impedance data sets by means of an equivalent circuit simulation to obtain the resistance values.

DC electrical conductivity measurements

Thin film devices with a top contact configuration were fabricated. Thin films were prepared, as described above, on Si(100) wafer with a 1000 nm insulating layer of thermally grown SiO_2 on the top. Au electrodes with a channel length of 50 μm, width of 1 mm, and thickness of 100 nm were fabricated on thin films by thermal evaporation with a metal mask. The *I-V* curves were collected with a high vacuum four probe instrument (Nagase Electric Instrumentation Co.) equipped with an Advantest R6245 Voltage Current Source Monitor. The samples were mounted on the top of an antivibration device with a temperature-controlled cryogenic chamber. All measurements were carried out in high vacuum achieved by a turbo-molecular pump.

References

1. E. Coronado, J. R. Galan-Mascaros, M. Monrabal-Capilla, J. Garcia-Martinez and P. Pardo-Ibanez, *Adv. Mater.*, 2007, **19**, 1359-1361.

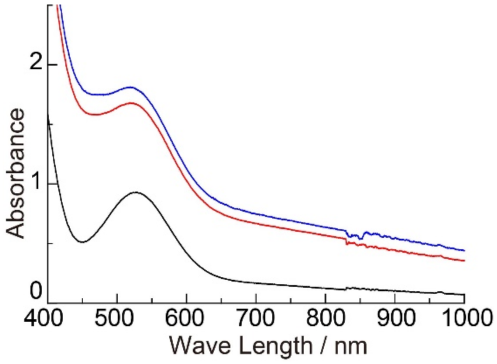

Fig. S1. UV-vis absorption spectra of **1** at 313 K before the heating cycles (black), after the 1st heating cycle (red), and after the 2nd heating cycle (blue).

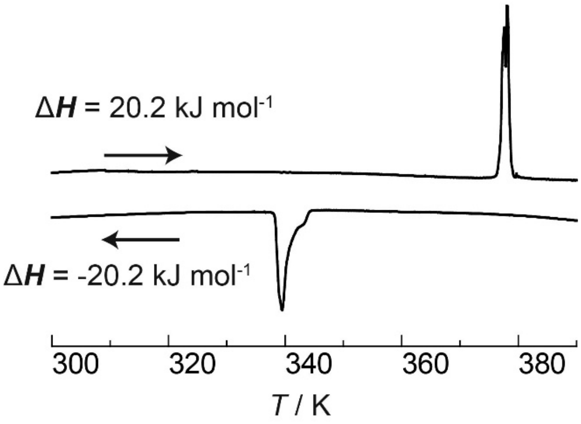

Fig. S2. DSC measurements for **1** during the 1st cycle under a nitrogen atmosphere with a 5 K min^{-1} scan rate.

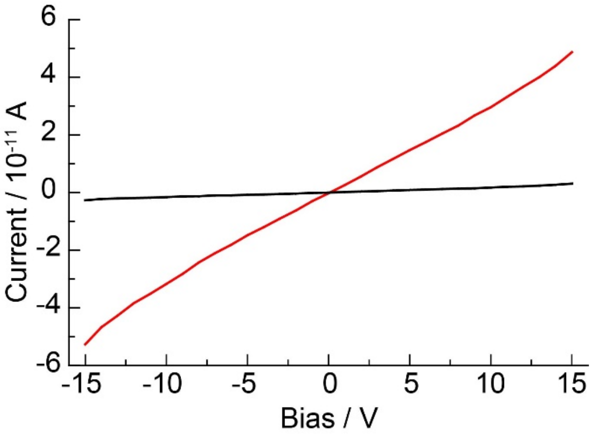

Fig. S3. *I-V* curves at 373 K for the devices fabricated using **1** (black) and **1**-SWCNT composite film (red). The current values are the averages of the sweep in the positive and negative bias directions.

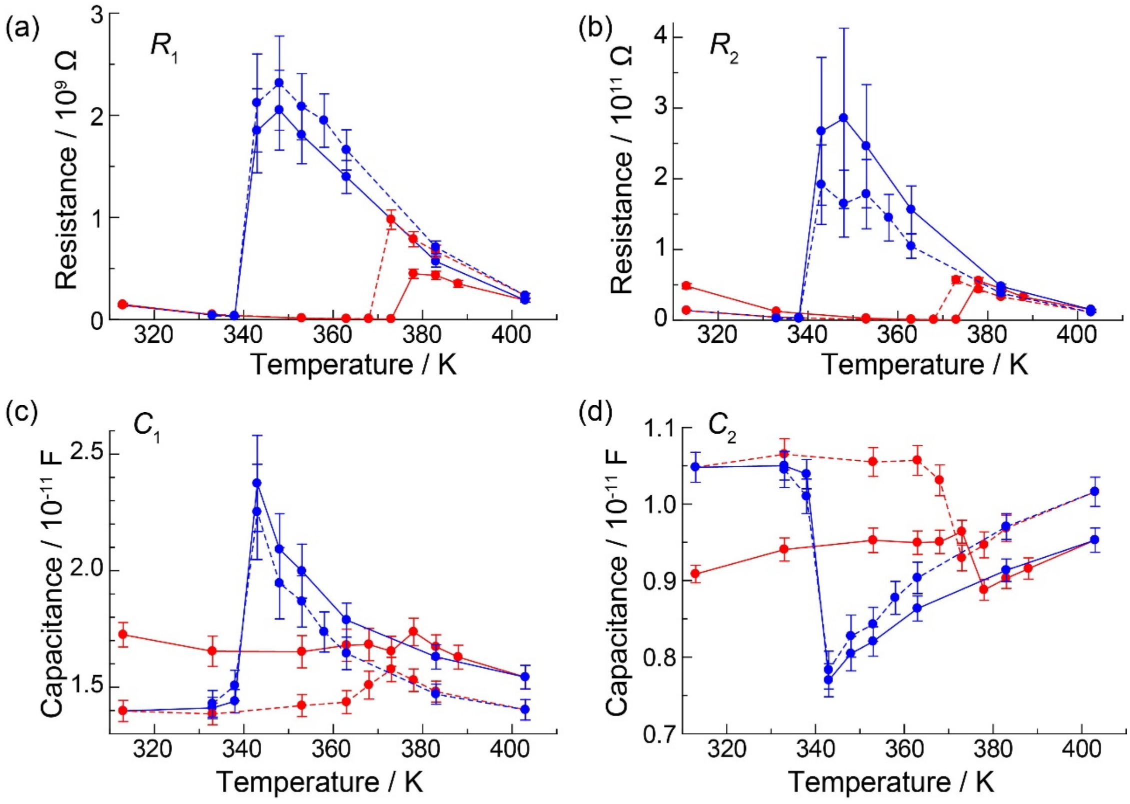

Fig. S4. Parameters of the equivalent circuit constructed from two resistances ((a) and (b)) and two capacitances ((c) and (d)) obtained from the curve fitting of the impedance spectra of **1**.

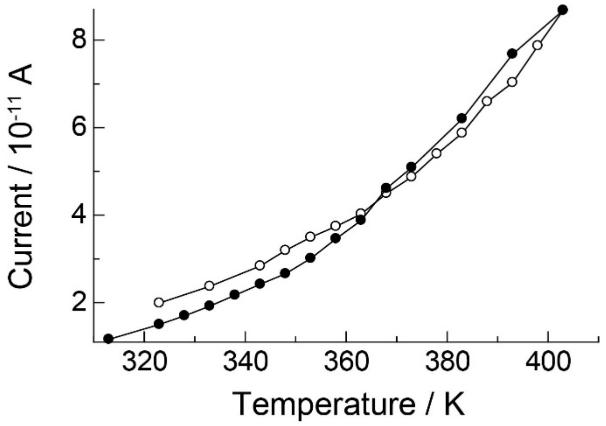

Fig. S5. Temperature dependence of the DC current at 15 V of the composite film in the first thermal cycle. Open and solid circles represent heating and cooling processes, respectively.

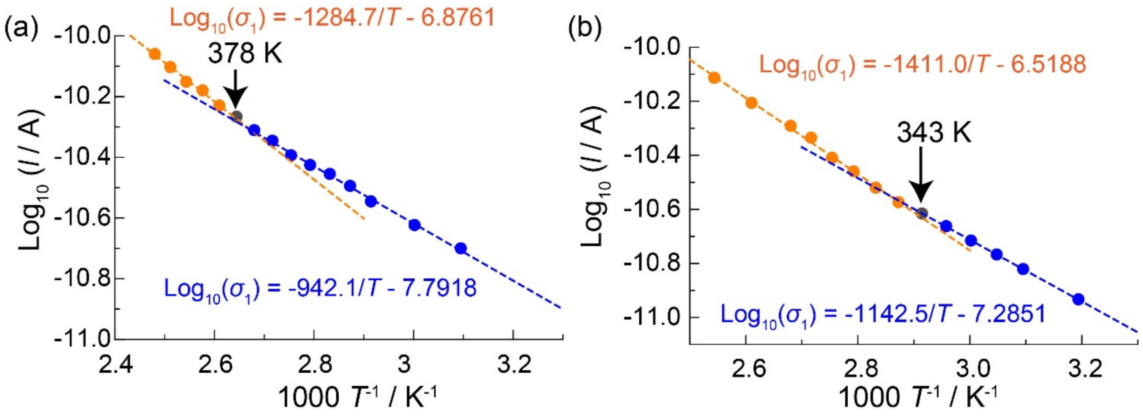

Fig. S6. Arrhenius plots of the DC current at 15 V for the composite film in the first heating (a) and first cooling (b) cycles. Blue and orange dashed lines show simulated values from Arrhenius equation in the LS and HS states, respectively.