Supplementary Information

Spin polarization in electrodeposited thin films of the molecule-based magnetic semiconductor $Cr_{5.5}(CN)_{12}\cdot 11.5\ H_2O$

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Experimental details

Experimental

Preparation of the Films: All reagents were purchased from Sigma-Aldrich and used without further purification. An electrochemical cell was charged with an aqueous solution (20 mL) containing $K_3[Cr(CN)_6]$ (5 mM) and $CrCl_3$ (7.5 mM).

Electrodeposited films of **1** were grown at a fixed potential (E = – 0.88 V vs Ag/AgCl reference electrode) on glass substrates (8x8 mm) coated with an evaporated Au layer of 90 nm thickness acting as the working electrode. The gold layer is evaporated using a mask which generates two stripes in the substrate each of them with a width of 500 μm and 6 mm length.

A Metrohm AUTOLAB potentiostat in coulometry mode was employed for depositing the colorless films. A Pt wire was used as a counter electrode. After preparation, films were rinsed with water and dried at room temperature. Films of different thickness were obtained by varying the time of deposition. The thicknesses were determined using an Ambios Technology XP-1 profilometer placed on a vibration isolation table.

The electrodeposited films are then transferred to the metal evaporator in order to deposite a 30 nm gold layer using the same mask as the one employed for the substrate. This second gold layer is evaporated perpendicular to the electrodeposited

films generating a cross-like geometry. In this way, the electrodeposited film is sandwiched between two gold electrodes for the magnetoresistance measurements. Anal. calcd for $C_{12}H_{23}Cr_{5.5}N_{12}O_{11.5}$: C 17.90, H 2.88, N 20.87; found: C 17.72, H 2.59, N 20.58. Powder X-ray diffraction of the electrodeposited films shows a typical cubic pattern corresponding to a Prussian blue structure with a = 10.42 Å. This pattern is independent of the film thickness (Figure S2).

ATR-IR spectroscopy: Infrared spectra of the electrodeposited films were recorded on a Nicolet 5700 FT-IR spectrometer using a Veemax II Specular Reflectance Accessory. (Figure S1)

AFM study: A Nanoscope Multimode (Veeco) atomic force microscope in tapping mode operation was used in the morphological study of the eletrodeposited films. RMS roughness and average particle size were analyzed by using WSxM4 4.0 Develop 13.0 software, developed by Nanotec Electronics S.L.

Magnetic measurements: Variable-temperature (applied field: 50 Oe) and field-dependent (T = 2 K) dc magnetization measurements were carried out in a Quantum Design MPMS Squid magnetometer. Several films of each thickness were cut in many pieces and were introduced in the sample holder with the applied magnetic field parallel or perpendicular to their surface. SQUID measurements were performed on samples electrodeposited on Mylar substrates coated with a evaporated gold layer of 100 nm thick. The magnetic susceptibility of the Au/Mylar substrates was measured independently in the same conditions and subtracted from the signal of the different films.

MOKE study: The magneto-optical characterization was performed with a self-made Kerr magnetometer. A He-Ne laser with a wavelength of 633 nm and an output power of 12 mW was used as the light source producing a nearly linearly-polarized light beam.

This beam was passed through a Glan-Laser Calcite polarizer with an extinction coefficient of 10^{-5}, which allows working with both s-polarized (electric field perpendicular to the plane of incidence) and p-polarized (electric field parallel to the plane of incidence) configurations.

The design of the electromagnets and the cryostat allows the use of longitudinal, polar and transverse geometries. The external magnetic field range in the polar configuration is ± 150 mT and in the longitudinal configuration 300 mT.

Magneto transports measurements. The temperature dependent conductivity (σ) and magnetoresistance (MR) have been measured using a standard two-probe method with Pt wire as leads in the same PPMS-9 equipment, in the temperature range between 100 K to 300 K using Keithley devices, a current source (model 2400) and an electrometer (model 6154). Electrical contacts were made with highly conducting silver paints.

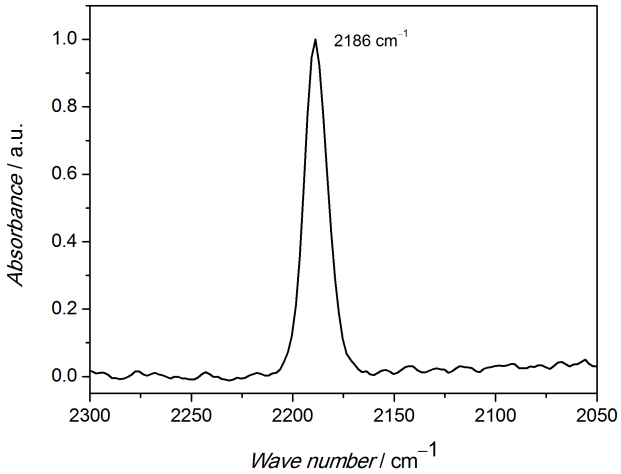

Figure S1. The IR spectrum of a thin film of **1** (80 nm thickness) after air exposure.

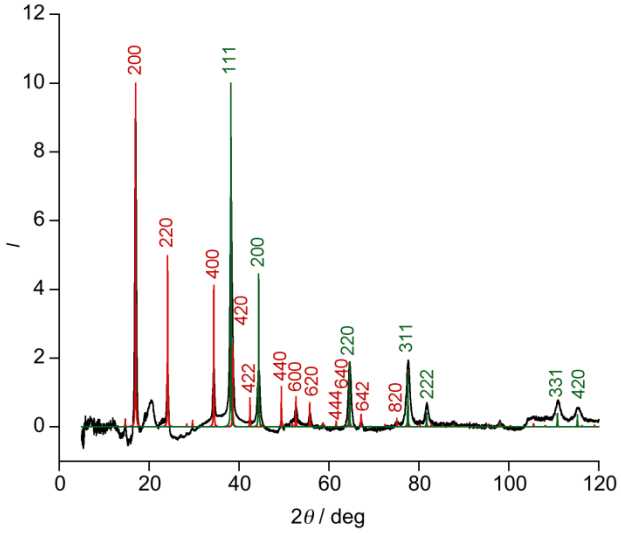

Figure S2. Powder X-ray diffraction (XRD) pattern (black line) of a thin film of **1** (time of electrodeposition: 100 s; thickness: 1500 nm). The simulated XRD patterns of a Prussian blue cubic structure with a = 10.42 Å (red line) and the Au metal cubic phase (a = 4.08 Å, green line) are shown for comparison.

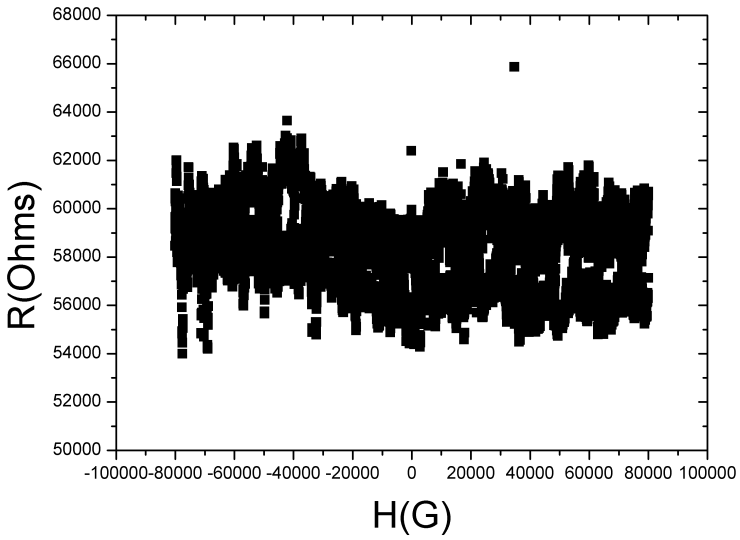

Figure S3. Resistivity measurement of the film 1 at 300 K. No resistivity changes can be addressed with the tuning of the external applied magnetic field.

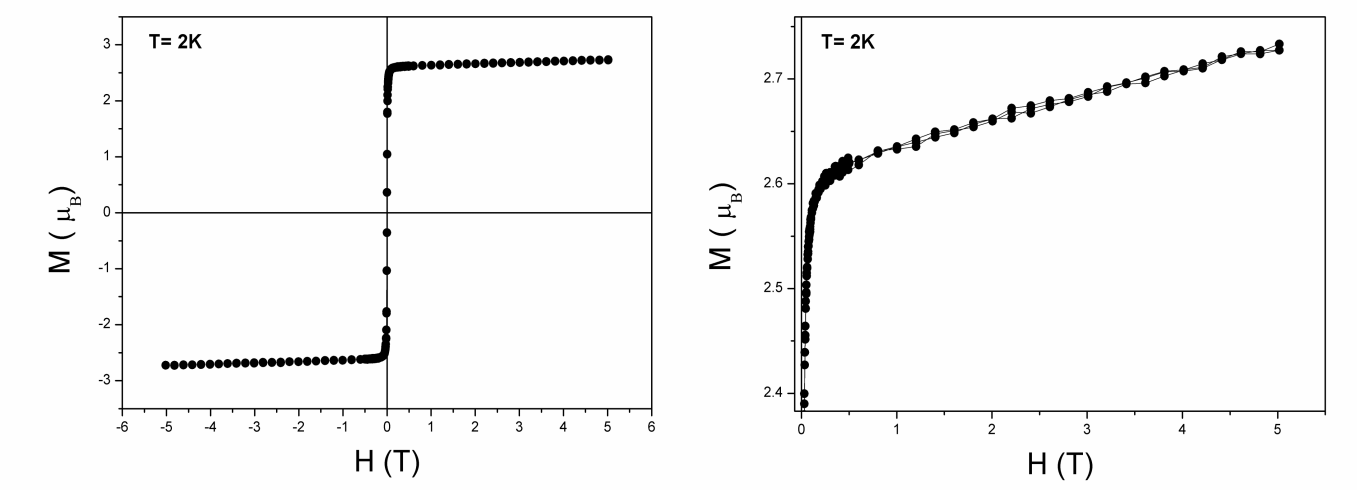

Figure S4. Hysteresis loop from SQUID at T=2K and at high magnetic fields. At the right part a zoom for higher magnetic fields, where a linear increase of magnetization versus applied magnetic field is observed for H>0.2 T.

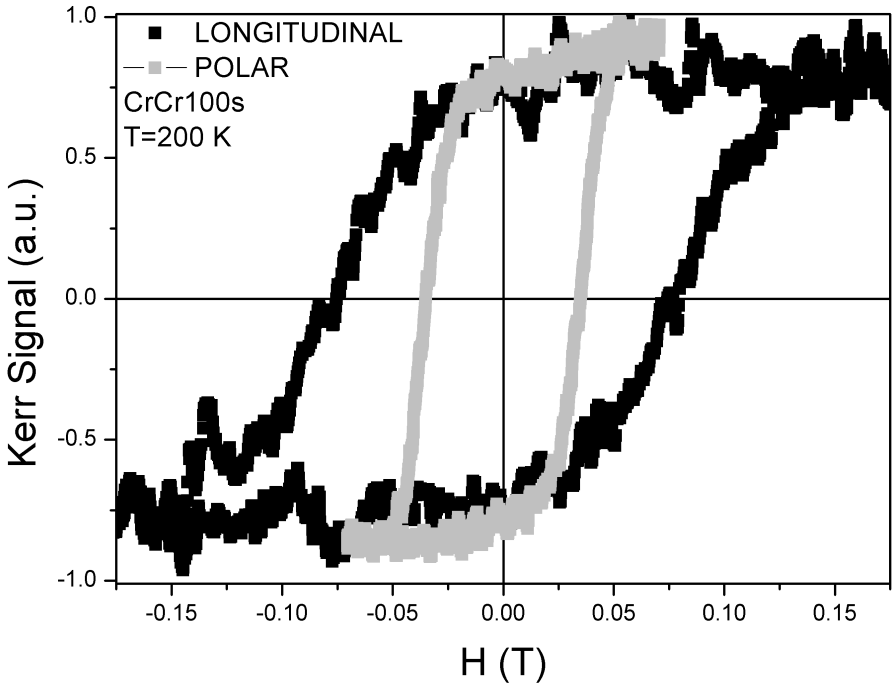

Figure S5. Hysteresis loop at T=200 K obtained by MOKE measurements in two different configurations, polar and longitudinal.

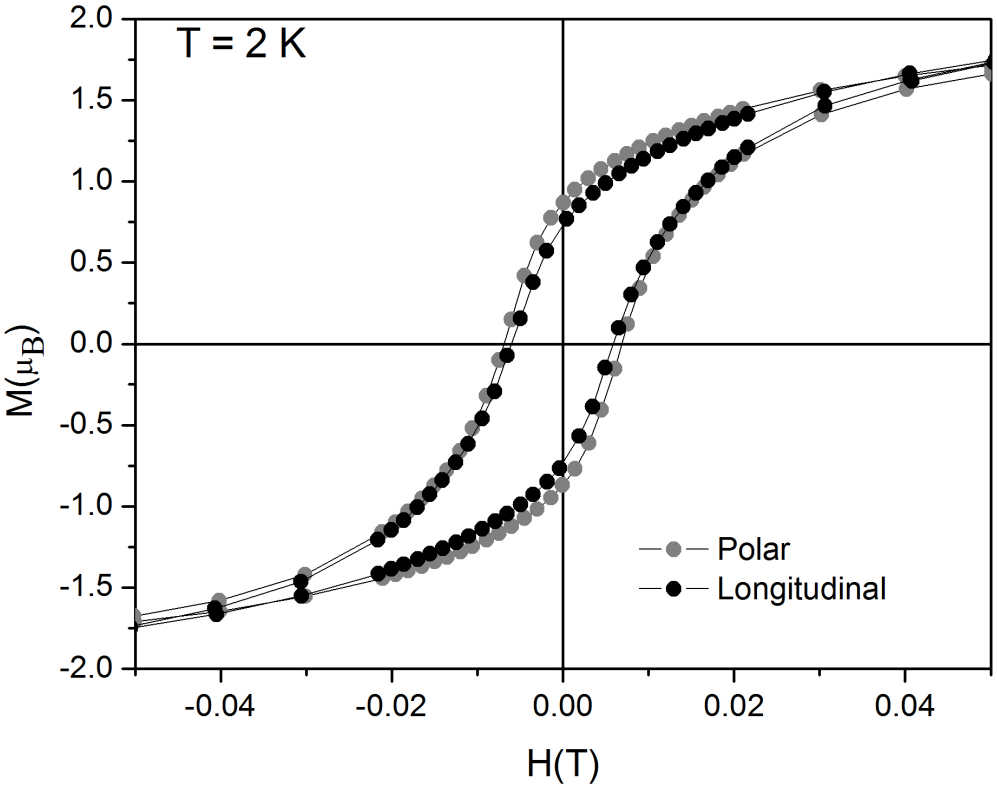

Figure S6. Hysteresis loops at T=2 K obtained by SQUID measurements in polar and longitudinal configuration.

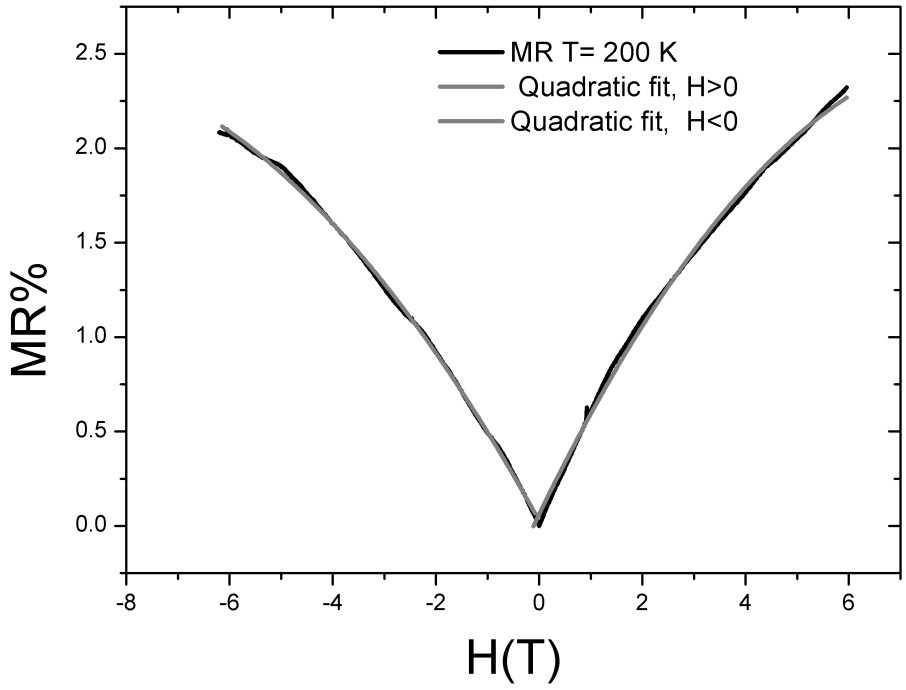

Figure S7. Analysis of the dependence of the magnetoresistance with the applied magnetic field. MR (H>0)= $-3.23\cdot10^{-10}\cdot x^2+5.63\cdot10^{-5}\cdot x+0.063$ and MR (H<0)= $-2.50\cdot10^{-10}\cdot x^2-4.94\cdot10^{-5}\cdot x+0.027$