Supporting information

A spin crossover (SCO) active graphene-Iron(II) complex hybrid material

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Experimental

Complex **1** was synthesized according to the literature procedure.[1] Dry 1, 2-dichloroethane (1, 2-DCE), acetone, and acetonitrile solvents were purchased from commercial sources. Graphene sheets dispersed in water was purchased from NanoIntegris as pure sheets^{TM}(MONO), batch# G24-103R, 1000mg in 1000 mL of the aqueous solution [B1UB150305].

Preparation of graphene-SCO (Gr-SCO) hybrid

To a 50 ml of Nanointegris aqueous graphene dispersion, 100 ml of acetone was added and the mixture was sonicated 30 seconds to enable mixing and left to stand overnight leading to precipitation of graphene sheets. The slurry was portioned into four 50 ml centrifuge tubes and centrifuged at 5000 rpm for 30 mins, the liquids were carefully decanted and fresh acetone was filled with the tubes and the slurry was centrifuged again; by this repeated washing and centrifugation cycle, 5 times, followed by drying under vacuum ca. 30 mg of graphene sheets were obtained. To prepare the Gr-SCO hybrid, 20 mg of the graphene sheets were redispersed in 50 ml of 1, 2-DCE solvent by sonicating the slurry for 30 mins. The dispersion was centrifuged at 500 rpm for 15 mins and ~ 3/4th of the *inky supernatant* was collected. To this 10 mg of complex **1** dissolved in 5 ml of acetonitrile was added and the mixture was stirred overnight under Argon atmosphere. The dispersion was centrifuged at 5000 rpm for 30 mins and ~ 3/4th of the supernatant was collected. The dispersions were portioned into 4 different test tubes and diethyl ether was layered above. Black sediments were obtained over a period of 1-2 weeks which were separated by filtering over a PTFE membrane and washed with cold 1:1 1, 2-DCE/ACN to remove the free complex **1**. Combination of four such preparations yielded ca. 10 mg of Gr-SCO hybrid which was dried under vacuum for 2 days and used for further experimentation. Two such samples were produced denoted as Gr-SCO-A and Gr-SCO-B. The sample Gr-SCO-A was utilized to perform TEM, IR, and Raman characterization experiments while both samples Gr-SCO-A and Gr-SCO-B were studied using SQUID magnetometry to check the reproducibility of the results. For the IR and Raman measurements, the ligand, the complex **1**, and the Gr-SCO hybrid (Gr-SCO-A sample) were resuspended in 1, 2-DCE.

Transmission Electron Microscopy (TEM)

The TEM experiments were carried out on a Cs-probe corrected Jeol 2100F microscope operated at 200kV and equipped with a Centurio EDS detector. For this investigation, low exposure times were employed in TEM (0.05s) and STEM (3µs/px) modes in an effort to avoid the beam-induced damage. Prior to its preparation for the TEM investigations, a small quantity of the specimen of interest was dispersed in ethanol in an ultrasound bath. The TEM grid was prepared by the direct deposition of a drop of this diluted suspension on a commercially holey carbon film deposited on a 300mesh Cu-grid.

Raman spectroscopy

Raman spectra of dried films of the ligand, complex **1,** and Gr-SCO-A hybrid were obtained using an InVia Renishaw spectrometer equipped with a CCD (charge coupled device) as a detector. All experiments were carried at a resolution of 1 cm^{-1} with an exposure time of 10 s and an excitation wavelength of 514 nm from an Argon STELLAR laser focused onto the sample through a 50× microscope objective. Raman spectra were recorded in the spectral region from 100 to 3000 cm^{-1} without accumulation procedure. It should be also noted that all Raman spectra shown in this study have been baseline corrected.

Magnetic and photomagnetic measurements

Magnetic measurements were performed on an MPMS-XL7 or MPMS-XL5 SQUID magnetometers (Quantum Design). For the standard magnetic measurement in the dark, the temperature dependent magnetization was recorded at B_{DC} = 0.1 T external magnetic field. The temperature sweeping rate was 1 K min^{-1} and it was the same for the cooling and heating modes. Gelatine capsules were used as sample holders in the temperature range 5 ↔ 400 K. For the photomagnetic experiments, a small amount of sample, complex **1** or Gr-SCO hybrid, (ca. 0. 1 mg) was introduced onto transparent tape and mounted into the sample holder. After cooling to 10 K, the sample, now in the LS state was irradiated (λ = 637 nm; 10 mW cm^{-2}) and the change in magnetization at B_{DC} = 1 T was followed. Upon reaching the saturation point, the light was switched off, the temperature was increased at a rate of 0.3 K min^{-1}, and the magnetization was measured at 1 K intervals. T(LIESST) value was determined from the minimum of the $\partial(\chi T)/\partial T$ *vs T* curve for the thermally induced relaxation process.

Fourier transformed infrared spectroscopy

The ATR-FTIR measurements of the ligand, complex 1 and the Gr-SCO-A were performed in the spectral range from 2000 to 800 cm^{-1} on an ATR (attenuated total reflection) Harrick crystal Diamond Prism). 2 μl of each sample was deposited in order to obtain a film on the diamond crystal.

The temperature dependent measurements were performed between 700 and 50 cm^{-1}. 5 μl of each sample were air-dried on a 2 mm thick polyethylene (PE) window, placed in a copper sample holder and mounted on the cold finger of a closed cycle Helium-cryostat (Model DE-202 AE, Advanced Research Scientific, Allentown, PA, USA). The temperature was measured close to the sample with a silicon diode (Scientific Instruments Calibration, precision of ± (0.5 K)). The temperature was regulated in the 294-50 K range with a heating resistor monitored by a digital temperature controller (Model 9700-1-1, Scientific Instruments, West Palm Beach, FL, USA).

Data in both the mid IR and the far IR were measured with a Vertex 70 instrument from Bruker (Karlsruhe, Germany). The spectrometer was purged with dry air in order to avoid contributions from humidity in the spectra. The optics and parameters were adapted for the different spectral ranges as follows: In the mid IR, from 2000 to 800 cm^{-1}, a detector mercury cadmium telluride (MCT) was used and the scan velocity was 40 kHz. Three spectra with resolution of 4 cm^{-1} (256 scans) were averaged for each sample. Baseline correction was applied to the absorption spectra obtained on the ATR mode (see Figure S5). In the far IR, from 700 to 50 cm^{-1}, a deuterated triglycine sulfate (dTGS) detector was used with a scan velocity of 2.5 kHz. For each sample, five spectra with a resolution of 4 cm^{-1} (128 scans) were averaged. The far IR spectra measured in a temperature dependent way were smoothed with 9 points and a straight baseline correction was applied. Then, the PE window absorption was interactively subtracted from the temperature dependent data (see Figures S6-S7).

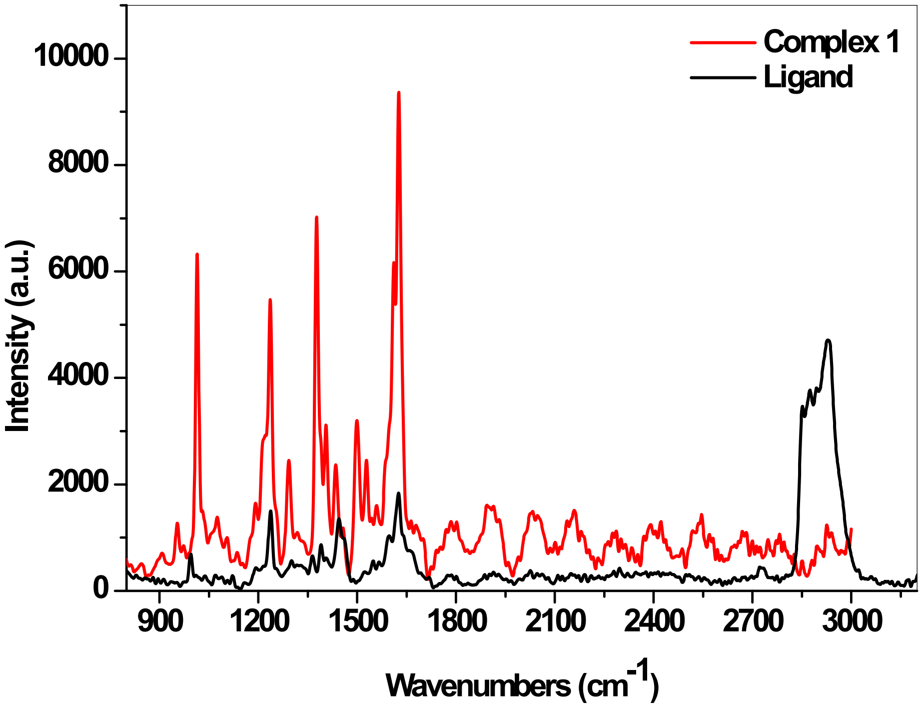

Figure S1. Raman spectra of the complex **1** and ligand. The excitation laser wavelength (λ) is 514 nm.

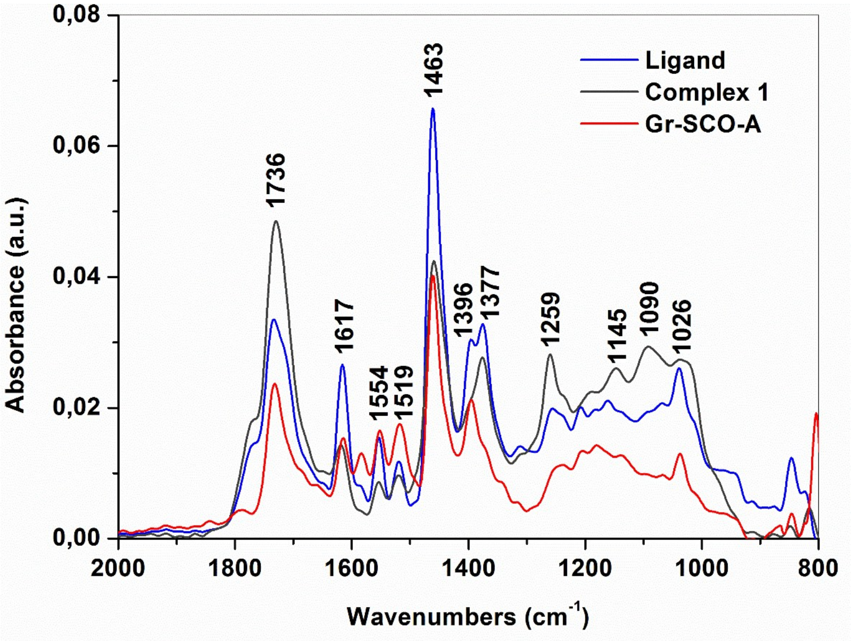

Figure S2. ATR-IR spectra on diamond crystal of the ligand, complex **1** and Gr-SCO-A as dry films. The spectrum of the Gr-SCO-A was multiplied by factor 5 for better visualization.

Table 1. Infrared bands of the ligand, complex 1 and Gr-SCO-A in 1, 2-DCE and their vibration assignment[2]. The following abbreviations have been used: ν: stretching, δ: scissoring, s: symmetric, as: anti-symmetric.

Wavenumber (cm^{-1})	**Assignments**
1736	ν(C=O)
1617, 1554	ν(COO$^-$)as
1519, 1554, 1617	ν(C=C-C), aromatic ring stretching
1463	δ(CH$_2$)
1396, 1377	ν(COO$^-$)s, ν(CN) aromatic tertiary amine
1145	ν(CO-O-C)as, ν(C-O-C) alkyl-substituted ether, C-O stretching.
1090	ν(CO-O-C)s
1026, 1090, 1145	δ(C-H), aromatic C-H in plane bending (several)

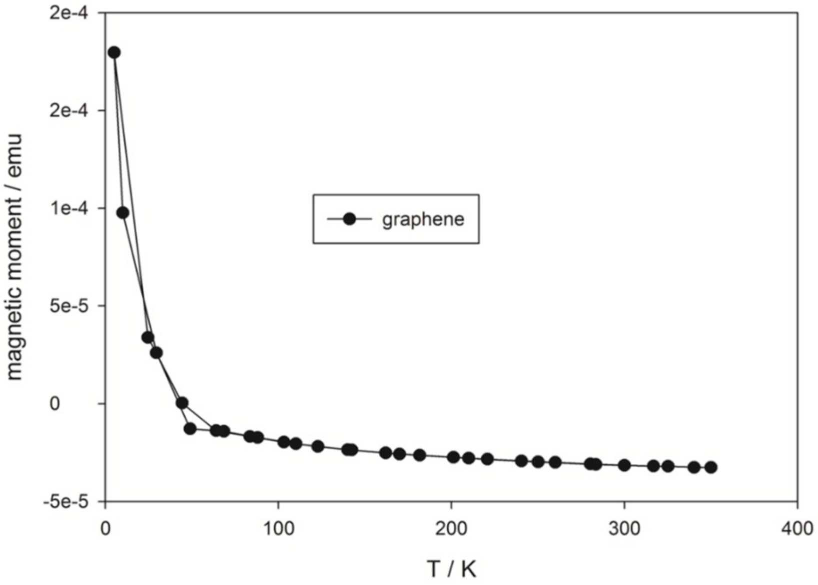

Figure S3. Variable temperature magnetic susceptibility of graphene sheets utilized to fabricate Gr-SCO hybrids.

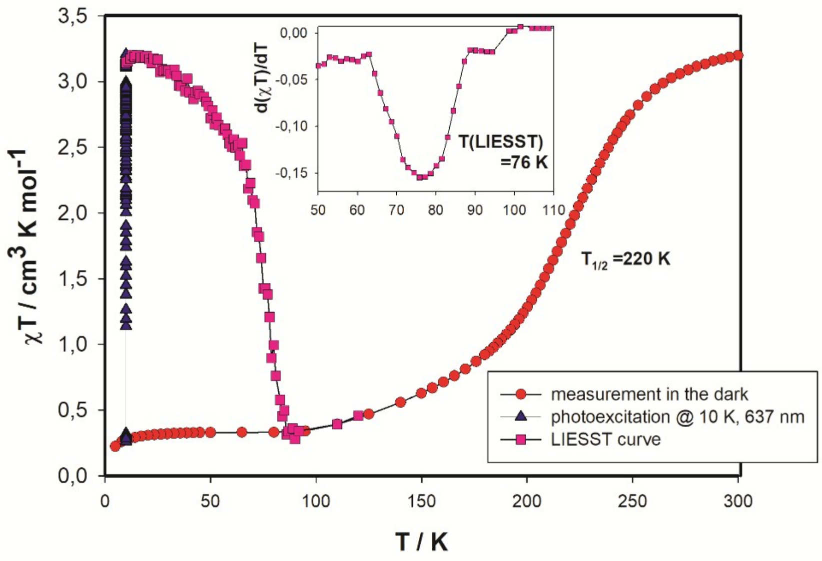

Figure S4. χ_mT vs. T and LIESST plot of complex **1**.

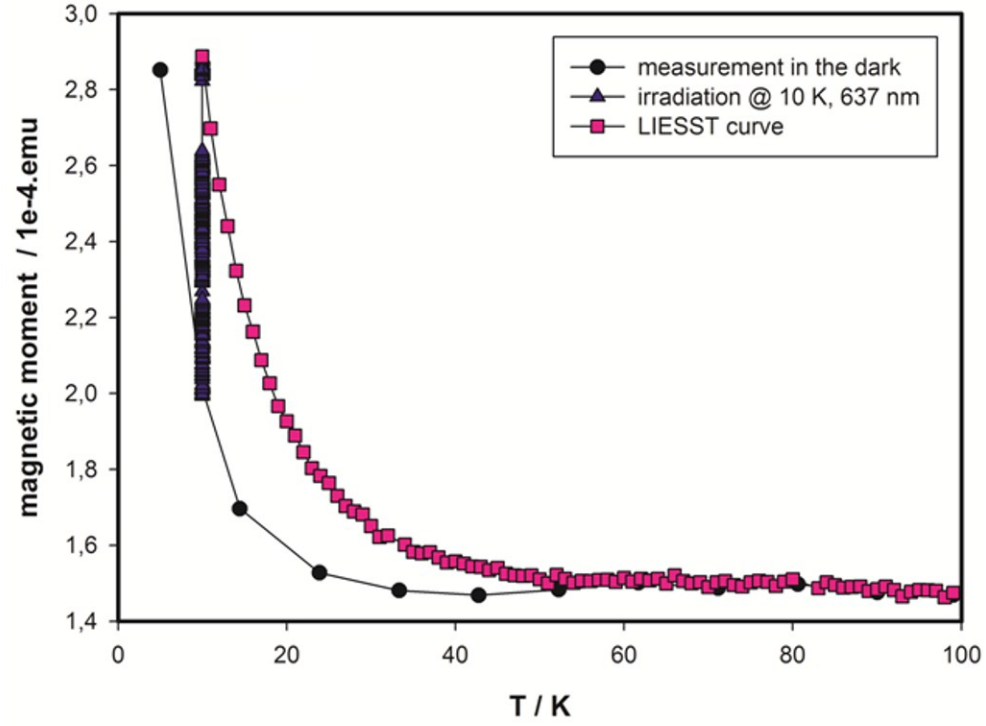

Figure S5. LIESST characteristics of hybrid Gr-SCO-A.

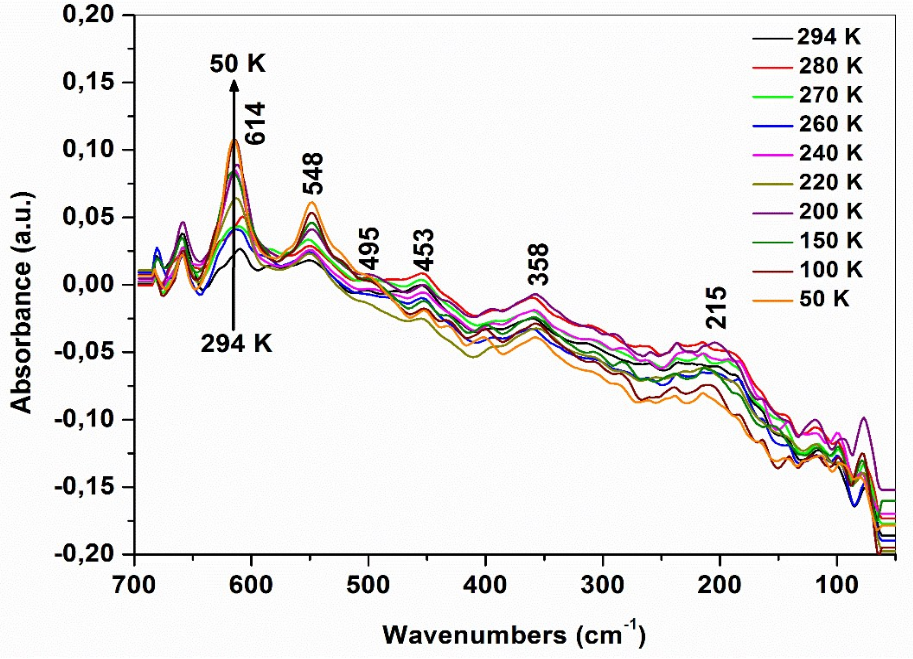

Figure S6. Temperature dependent far infrared absorbance spectra of the SCO complex **1** from 294 K to 50 K. The arrow shows the signal shift observed for the transition from 294 K to 50 K.

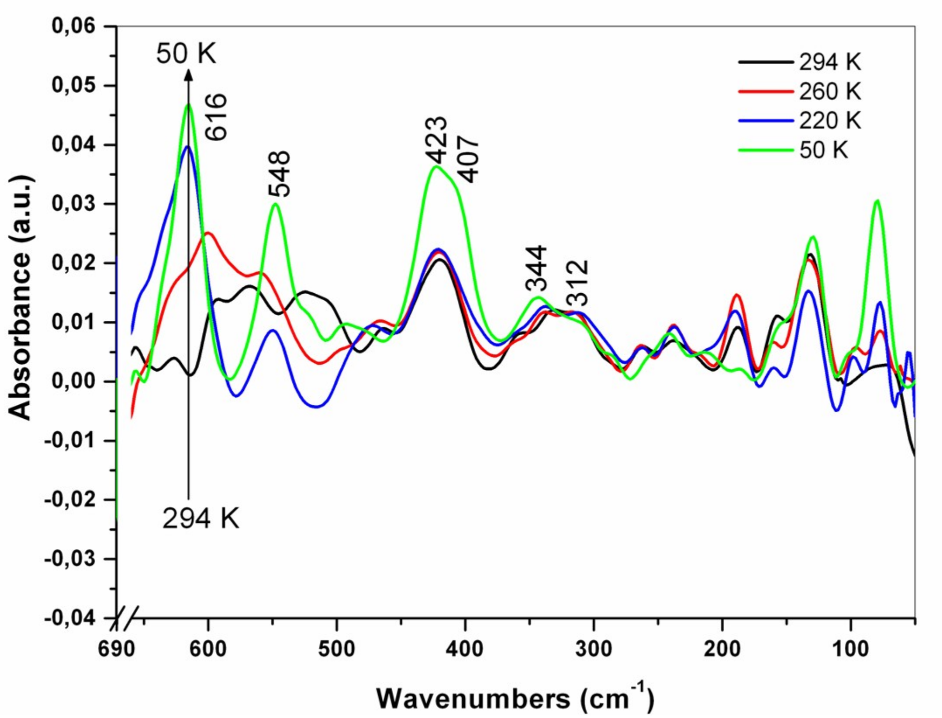

Figure S7. Variable temperature far infrared absorbance spectra of the ligand. The arrow shows the signal shift observed for the transition from high to low temperature.

References

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2 M. Jackson and H. H. Mantsch, *Crit. Rev. Biochem. Mol Biol.,* 1995, **30,** 95-120.