

## Supporting Information

### **A Hybrid Organic-Inorganic Molecular Daisy Chain**

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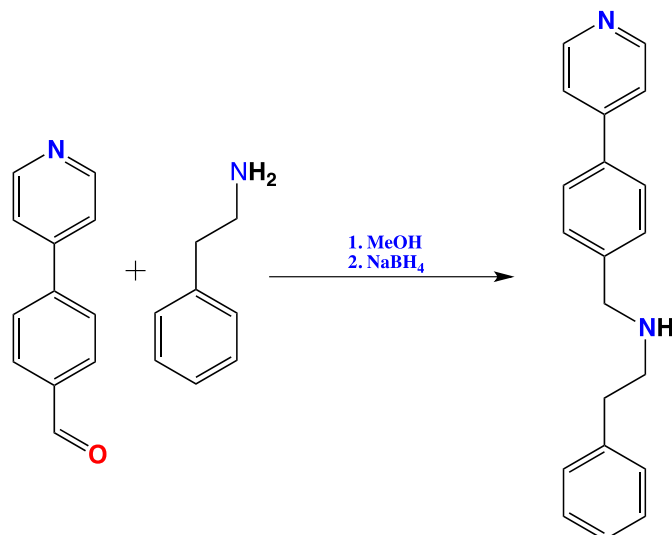
#### **Experimental Details**

Unless stated otherwise, all reagents and solvents were used without further purification. The syntheses of the hybrid organic-inorganic rotaxanes were carried out in Erlenmeyer Teflon® FEP flasks supplied by Fisher. Column chromatography was carried out using Silica 60A (particle size 35-70 µm, Fisher, UK) as the stationary phase, and TLC was performed on precoated silica gel plates (0.25 mm thick, 60 F254, Merck, Germany) and observed under UV light. NMR spectra were recorded on Bruker AV 400 instrument. Chemical shifts are reported in parts per million (ppm) from low to high frequency and referenced to the residual solvent resonance. ESI mass spectrometry and microanalysis were carried out by the services at the University of Manchester. 4-pyridine phenylaldehyde was obtained according to reference *Angew. Chem. Int. Ed.* 2010, **49**, 3757 –3761.

#### **Synthesis of organic thread 2**

To a solution of 4-pyridine phenylaldehyde (0.7 g, 3.8 mmol) in 30 mL of methanol, phenylethylamine (0.48 mL, 3.8 mmol) was added and the reaction mixture was refluxed for 3 hr under nitrogen atmosphere, allowed to stir at room temperature overnight. NaBH<sub>4</sub> (5 equivalents) was added and reaction mixture was stirred during 12 h under nitrogen atmosphere. The reaction was quenched with water and the solvent was evaporated. The solid was extracted with chloroform, washed with water and dried over anhydrous magnesium sulphate and the solvents evaporated. A light yellow liquid was obtained in 75 % yield (0.85 g) as compound **L**. LR-ESI-MS (sample dissolved in MeOH, run in MeOH): m/z = 287 [M-H]<sup>-</sup>. HR-ESI-MS (TOF): m/z = 287.1540 [M-H]<sup>-</sup> (calc. for C<sub>20</sub>H<sub>19</sub>N<sub>2</sub> 287.1548 [M-H]<sup>-</sup>). <sup>1</sup>H-NMR (400 MHz, 293K, CDCl<sub>3</sub>): δ = 2.81-2.93 (m, 4H), 3.98 (s, 2H), 7.2-7.3 (m, 5H), 7.5 (d, 2H, J = 7.9 Hz),

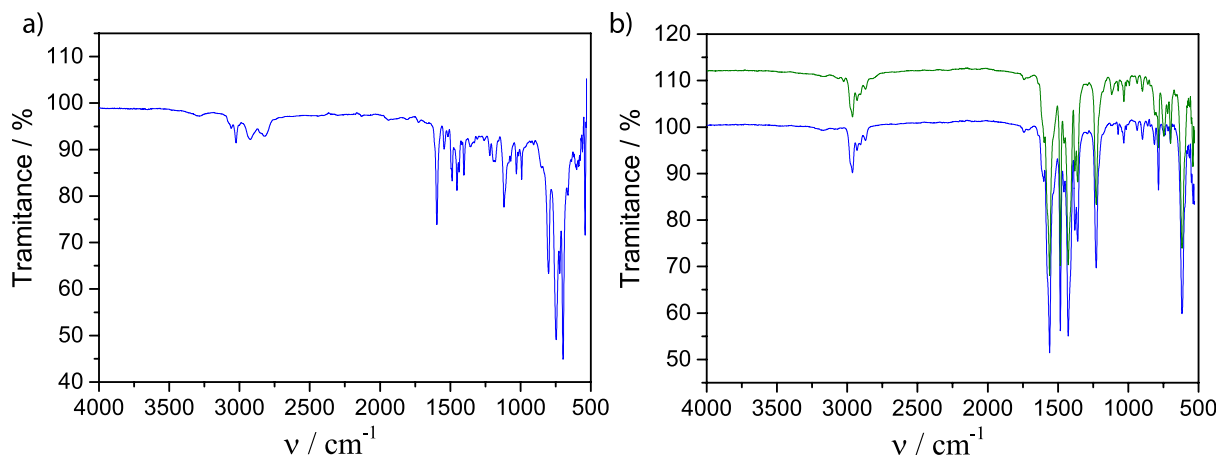
7.6 (*d*, 2H, *J* = 8.7 Hz) 7.7 (*d*, 2H, *J* = 7.9 Hz), 8.7 (*d*, 2H, *J* = 8.7 Hz). <sup>13</sup>C NMR (75 MHz, 293K, CDCl<sub>3</sub>): δ = 33.5, 49.3, 53.6, 121.1, 121.2, 123.2, 123.6, 125.2, 128.2, 129.0, 129.4, 133.5, 136.9, 142.8, 150.1, 150.5, 167.7, IR (cm<sup>-1</sup>): 3285.5, 3063.5, 3023.1, 2921.9, 2818.0, 1594.7, 1542.3, 1487.5, 1448.8, 1437.8, 1401.9, 1114.9, 1032.4, 988.3, 803.4, 745.4, 695.7.



**Scheme 1.** Schematic representation of synthesis **L**.

### Synthesis of {Cr<sub>6</sub>Zn<sub>2</sub>(μ-F)<sub>8</sub>(O<sub>2</sub>C<sup>t</sup>Bu)<sub>15</sub>(N<sub>2</sub>C<sub>20</sub>H<sub>21</sub>)<sub>2</sub>} **1**

Pivalic acid (20.0 g, 195 mmol), **L** (0.5 g, 1.7 mmol), CrF<sub>3</sub>·4H<sub>2</sub>O (2.1 g, 12 mmol) and ZnCO<sub>3</sub> (1.8 g, 3.4 mmol) were heated at 140°C with stirring in a Teflon flask for 1 h and thereafter the temperature of the reaction was increased to 160°C for 21 h. The flask was cooled to room temperature, and then acetonitrile (35 mL) was added while stirring. The green microcrystalline product was collected by filtration, washed with a large quantity of acetonitrile, dried in air, washed with acetone and toluene, and then the remaining solid was extracted with THF to afford the desired product as a green crystalline solid (1.5 g) in 35 % yield. Elemental analysis (%) calcd for C<sub>190</sub>H<sub>312</sub>Cr<sub>12</sub>F<sub>16</sub>N<sub>4</sub>Zn<sub>4</sub>O<sub>60</sub>: Cr 12.99, Zn 5.45, C 47.53, H 6.55, N 1.17; found: Cr 12.79, Zn 5.52, C 47.74, H 6.75, N 1.21. X-ray quality crystals were obtained for **3** by recrystallization from hot toluene after 3 days. IR (cm<sup>-1</sup>): 2962.5, 2929.8, 2905.6, 2870.5, 1562.4, 1485.0, 1428.1, 1377.8, 1359.6, 1227.2, 782.5, 618.1.



**Figure S1.** (a) Solid state infrared spectrum of **L**; (b) solid state infrared spectrum of **1** of powder (green) and crystals (blue).

## Crystallography

The data of **1** was collected on Agilent SuperNova CCD diffractometer with MoK $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The structure was solved by direct methods and refined on  $F^2$  using SHELXTL in Olex2. CCDC 1034374 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

The data collection of this sample was performed at 270 K, using vacuum grease due to instability of the sample at lower temperatures. Exposure time of 150 sec/frame were used during the data collection using molybdenum source, however even after such long exposure time, no reflections were observed above 0.9 Å. The data was therefore trimmed to this value.

A large degree of disorder was encountered during the solution of the data, probably due to thermal movement, consequence of the collection at high temperature. Most pivalates groups were split in two parts and restrained/constrained using RIGU, SADI, DANG and DFIX commands. Similarly the phenyl and two methanediyl groups were also split and modelled accordingly. The structure contains large solvent accessible voids. However, the location of discrete solvent molecules could not be determined by simple refinement. A red alert due to big solvent Voids was encountered during the check cif., we therefore SQUEEZE the data. A total of 508 electron counts were obtained, which correspond to approximately 10 toluene solvent molecules (50 electron counts per molecules). The molecular formula is

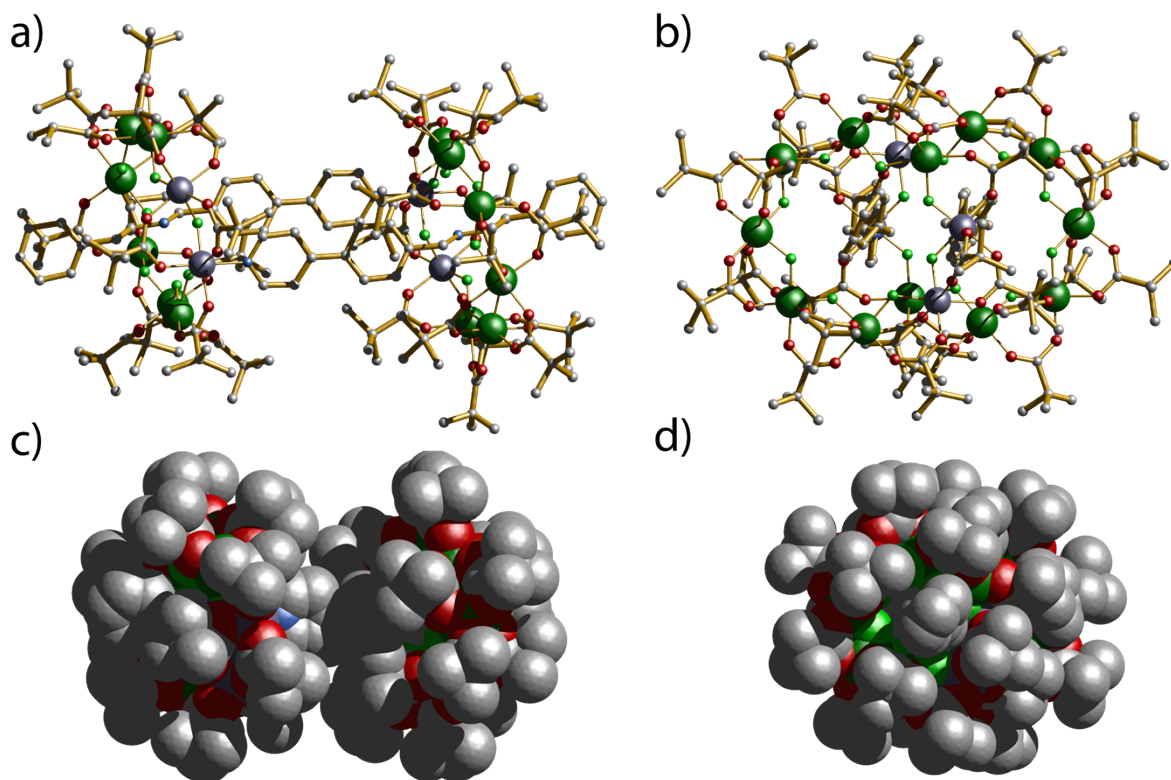
below amended to take into account all solvent molecules. These solvent molecules are not included in the final .cif, therefore the molecular formula, density and other atom-dependent values might not be completely correct.

\_chemical\_formula\_moiety 'C<sub>95</sub>H<sub>157</sub>Cr<sub>6</sub>F<sub>8</sub>N<sub>2</sub>O<sub>30</sub>Zn<sub>2</sub>, 10(C<sub>7</sub>H<sub>8</sub>)'

\_chemical\_formula\_sum 'C<sub>165</sub>H<sub>237</sub>Cr<sub>6</sub>F<sub>8</sub>N<sub>2</sub>O<sub>30</sub>Zn<sub>2</sub>'

Due to the nature of the collection, missing some low angle data, the number of solvent molecule might not be completely accurate; therefore care must be taken when considering the number of solvent molecules obtained through the solvent masking procedure.

Crystal data for **1** [C<sub>95</sub>H<sub>156</sub>Cr<sub>6</sub>F<sub>8</sub>N<sub>2</sub>O<sub>30</sub>Zn<sub>2</sub>]: *Mr* = 2400.95, monoclinic, space group *P*2<sub>1</sub>/*c*, *T* = 270.1(2) K, *a* = 23.6326(12), *b* = 22.5386(11), *c* = 37.8111(15) Å, β = 126.954(3), *V* = 16094.2(14) Å<sup>3</sup>, *Z* = 4, ρ = 0.991 g cm<sup>-3</sup>, total data = 22942, *R*<sub>1</sub> = 0.0831 for *I* ≥ 2σ (*I*) and *wR*<sub>2</sub> = 0.2321.

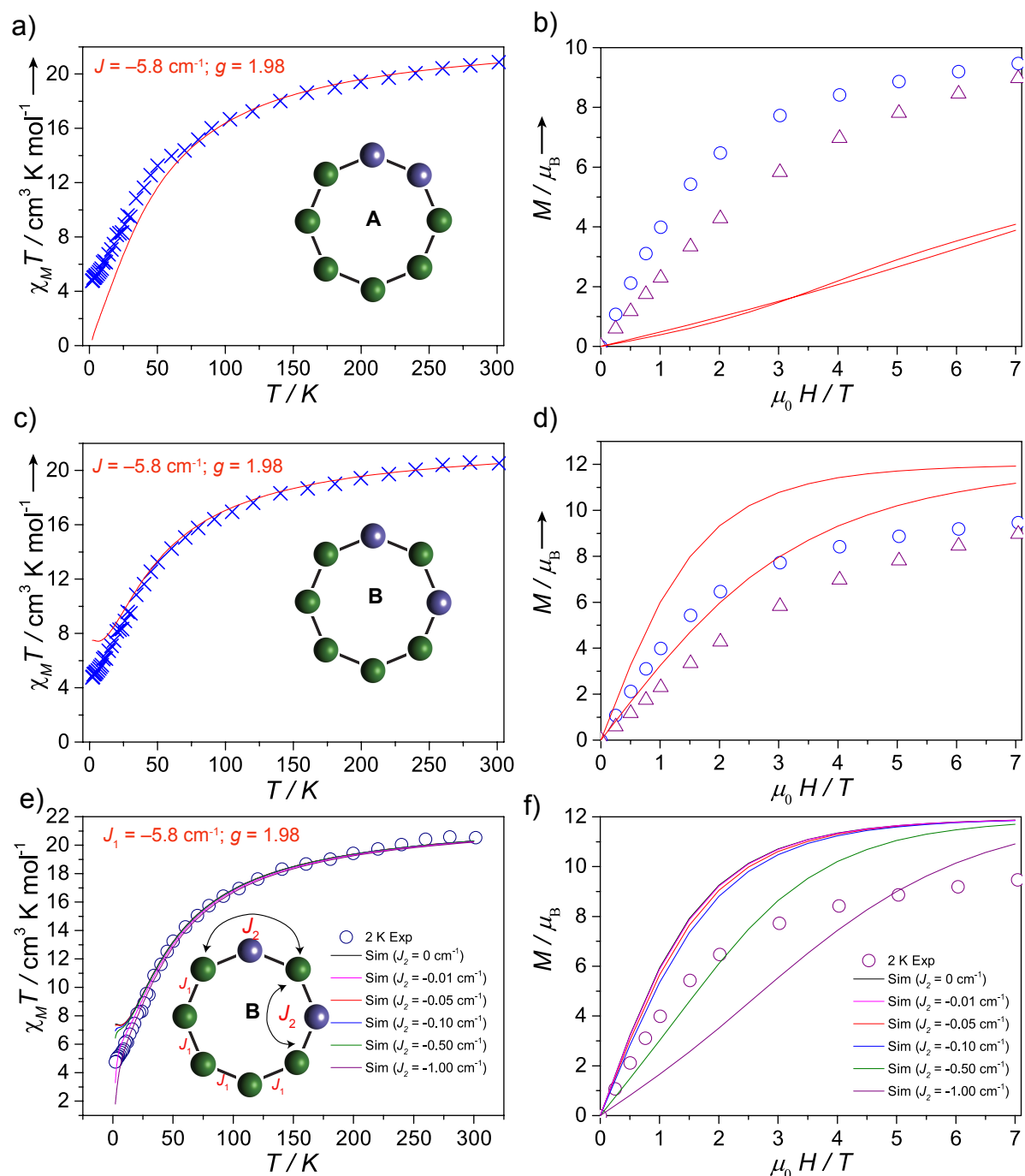


**Figure S2.** Crystal Structure of **1**, ball and stick representation (a) and (b); and space fill (c) and (d). Colour code: Cr, green; Zn, grey; F, yellow; O, red; C, grey; N, blue. H-atoms omitted for clarity.

### Magnetic measurements

The magnetic properties in the temperature range 1.8K-300K were performed on polycrystalline samples either constrained in eicosane or lastly powdered, using a

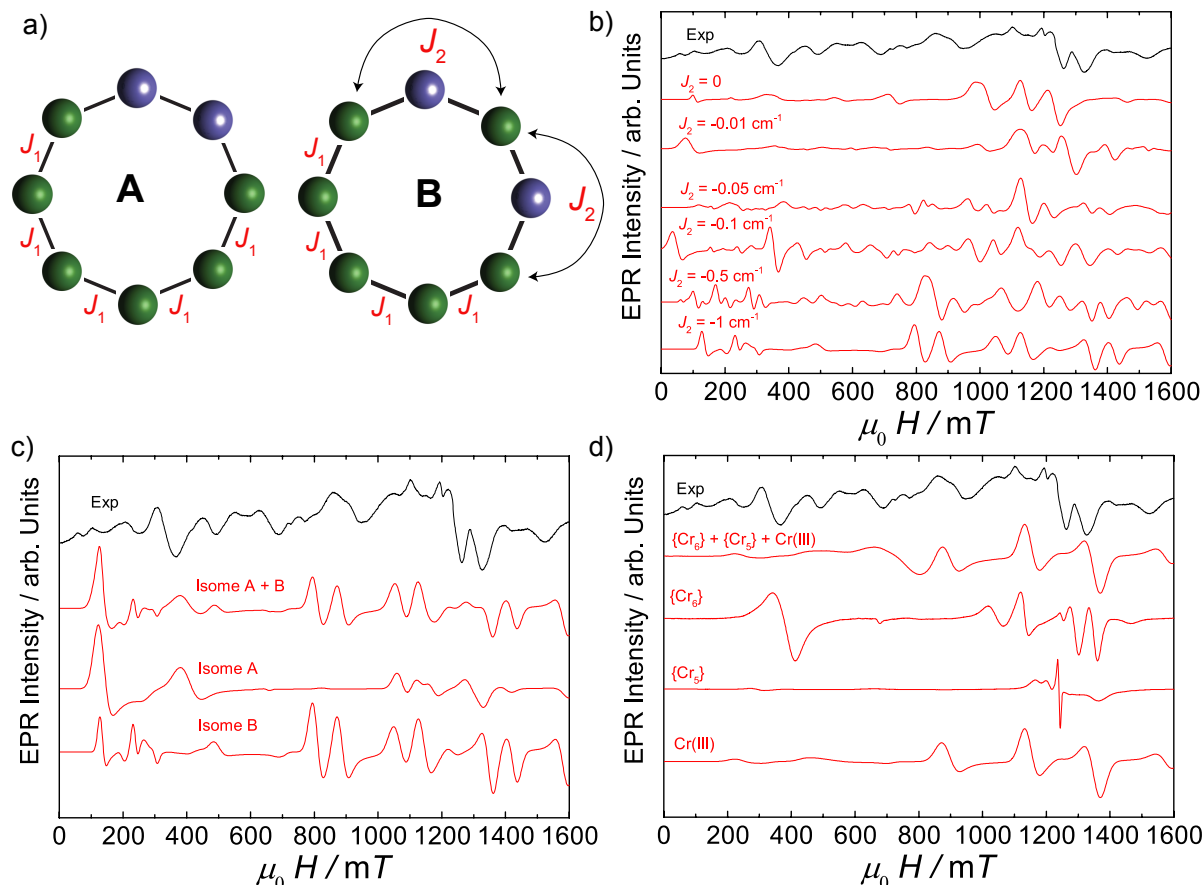
Quantum Design MPMS-XL7 SQUID magnetometer armed with a 7 T magnet. Data were corrected for the diamagnetism of the compounds (Pascal constants) and for diamagnetic contribution of eicosane and the sample holder.



**Figure S4.**  $\chi_M T$  vs.  $T$  and  $M/\mu_B$  vs.  $H$  for compounds 1, and simulation (red trace) for isomer: **A**, (a) and (b); **B**, (c) and (d). Simulations assuming long range Cr $\cdots$ Cr exchange interactions ( $J_2$ ) (e and f), using fix  $g$ -values and fix nearest neighbour exchange interaction ( $J_1$ ) i.e.  $g = 1.98$  and  $J_1 = -5.8 \text{ cm}^{-1}$ . As observed although the  $\chi_M T(T)$  simulations are not far from experimental data, the  $M/\mu_B$  vs.  $H$  is very far from agreement, suggesting that long range exchange interactions are not responsible for the magnetic behaviour.

## EPR measurements

Q-band (~35 GHz) spectra were recorded with a Bruker EMX580 spectrometer. The data were collected on polycrystalline powders at 5K using liquid helium cooling. Spectral simulations were performed using the EasySpin 4.5.5 simulation software.



**Figure S5.** (a) Schematic representation of isomers A and B; (b) Simulations for isomer B (ordered structure) using a  $g$ -value (1.98), a  $D = -0.34 \text{ cm}^{-1}$  a nearest neighbour exchange interaction ( $J_1 = -5.8 \text{ cm}^{-1}$ ) and a varying the long range exchange interaction ( $J_2$ ) as described in the graph. Conversely to SQUID data, EPR spectroscopy is extremely sensitive to small  $J_2$  variations, therefore the transitions observed in the experimental data not present in neither of the experimental  $\{\text{Cr}_6\}$ ,  $\{\text{Cr}_5\}$  and Cr(III) chains might be due to this small interactions; (c) Addition of simulated data for isomer A and B using 30% of isomer A and 70% of isomer B; (d) and added experimental data for  $\{\text{Cr}_6\}$ ,  $\{\text{Cr}_5\}$  and Cr(III) chains employing 30% of  $\{\text{Cr}_6\}$  and 70% of  $\{\text{Cr}_5\}$  and Cr(III). As observed neither of the added set of data represents well the experimental data. The reason being that EPR spectroscopy is a technique that is based upon transition between the  $m_J$  states of the electronic structure of the material, and the intensity of the signals depend on the transition probability. In this sense, although a weighting ratio of 3:7 was obtained from magnetometry data, these values do not convey the full information to get more insight into the nature of the isomers from the EPR point of view. This due to the intensity of the signal (transition probability) of the EPR spectra is not directly related to the weighting ratio of the isomers.