

SUPPORTING INFORMATION FOR

Synthesis and Size Control of Iron(II) Hexacyanochromate(III) Nanoparticles and the Effect of Particle Size on Linkage Isomerism

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This supporting information contains: **(1)** Magnetic measurements and FTIR at $t = 0$ and $t = 91$ hours; **(2)** Solid state second order kinetic model; **(3)** Low-field region of magnetization, M , as a function of applied field, $\mu_0 H$, showing the coercive field; **(4)** Magnetization, M , as a function of temperature, T ; **(5)** Magnetic measurement procedures; **(6)** Activation energy as a function of particle size; **(7)** Particle size distribution.

1. Magnetic measurement and FTIR at $t = 0$ and $t = 91$ hours.

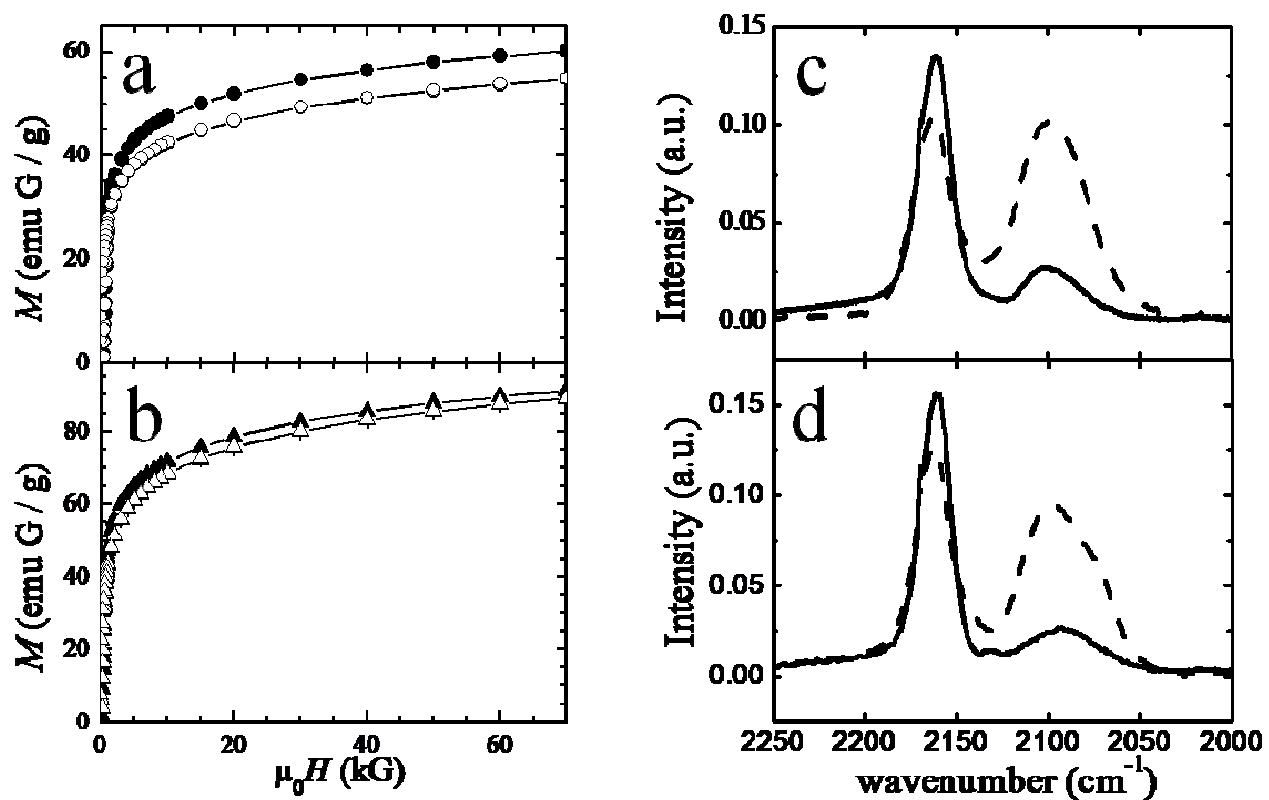


Figure S1. (a) Magnetization, M , as a function of applied field, $\mu_0 H$ for the 30 nm nanocrystals (7) (●) initial and (○) after 91 hours at RT. (b) Magnetization, M , as a function of applied field, $\mu_0 H$ for the bulk (1) (▲) initial and (△) after 91 hours at RT. FTIR spectra for the 30 nm nanocrystals (7) (c) and bulk (1) (d). The solid line corresponds to the compound immediately after synthesis and the dashed line to the same sample after 91 hours at RT.

2. Solid-state second order kinetic model.

The relation used to plot the solid lines in Figure 4 is derived as follow, assuming a second order rate kinetics:

Second order rate equation:

$$\frac{1}{[A]} = \frac{1}{[A]_0} + kt \quad , (1)$$

Arrhenius law:

$$k = \alpha e^{-\frac{E_a}{RT}} \quad , (2)$$

Combining (1) and (2) :

$$\frac{1}{[A]} = \frac{1}{[A]_0} + \alpha e^{-\frac{E_a}{RT}} t \quad , (3)$$

Equation (3) modified for solid-state $A \rightarrow B$ reaction reaching an equilibrium with finite initial quantity of A (A_i) and finite equilibrium quantity of A (A_e) gives:

$$A = \left(\frac{1}{A_i} + \alpha e^{-\frac{E_a}{RT}} t \right)^{-1} + A_e \quad , (4)$$

Where A is the percentage of chromium cyanide bonds, A_i is the percentage of chromium cyanide bond that have been isomerized at equilibrium ($A_i = A - A_e$), α is pre-exponential factor commun to the bulk and nanoparticles. E_a is the energy of activation, R ideal gas constant, T the temperature and A_e the percentage of chromium cyanide at equilibrium.

Table S1 Parameters used with equation (4) to plot the solid lines in figure 4.

	A_I (%)	α	A_e (%)	R ($J \cdot K^{-1} \cdot mol^{-1}$)	T (K)	E_a ($J \cdot mol^{-1}$)
30nm	9.9	2×10^5	58.73	8.314	298	21000
Bulk	3.6	2×10^5	64.02	8.314	298	46000

3. Low-field region of magnetization, M , as a function of applied field, $\mu_0 H$.

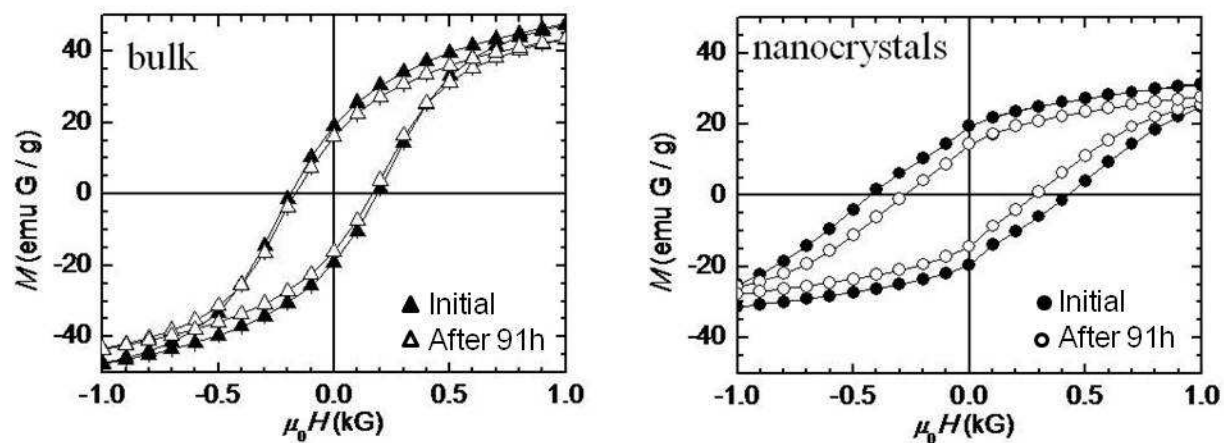


Figure S2. Left: Low-field region of the magnetization, M , as a function of applied field, $\mu_0 H$ for the bulk (1) (\blacktriangle) initial and (\triangle) after 91 hours at RT. Right: Low-field region of the Magnetization, M , as a function of applied field, $\mu_0 H$ for the 30 nm nanocrystals (7) (\bullet) initial and (\circ) after 91 hours at RT.

4. Magnetization, M , as a function of temperature, T .

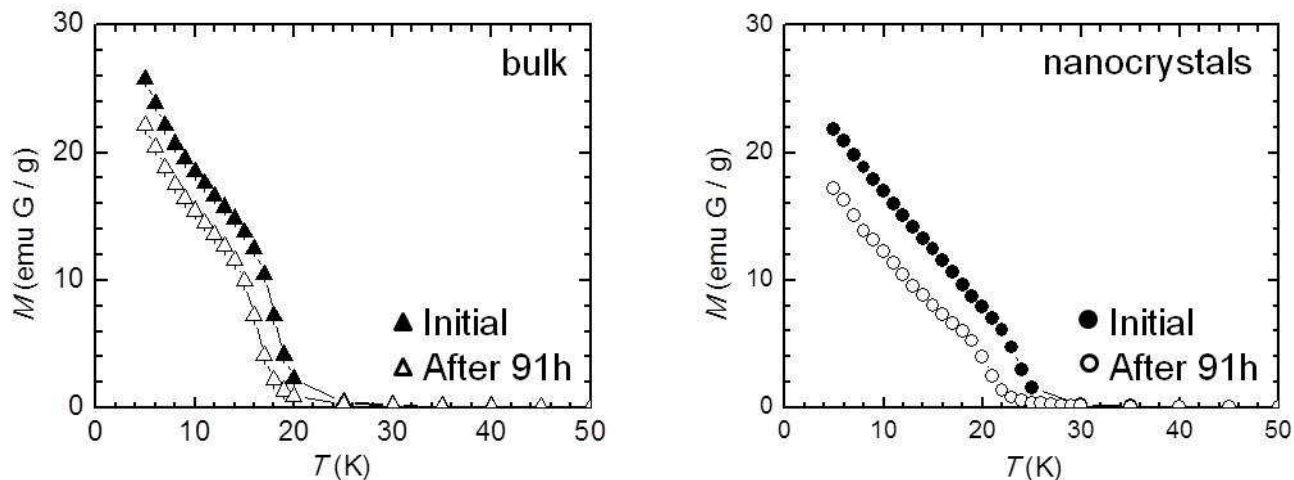


Figure S3. Left: Magnetization, M , as a function of temperature, T for the bulk (**1**) (\blacktriangle) initial and (\triangle) after 91 hours at RT. Right: Magnetization, M , as a function of temperature, T for the 30 nm nanocrystals (**7**) (\bullet) initial and (\circ) after 91 hours at RT.

5. Magnetism measurement procedures.

The samples, 15.91 mg for the bulk and 10.45 mg for the nanocrystals, were loaded into the SQUID and immediately cooled. After reaching 5 K, the sample was centered in an applied field of 100 G, and data were obtained while sweeping the field from 0 to 70 kG, 70 kG to -70 kG, and -70 kG to 70 kG (Figure S1 and figure S2). After the hysteresis loop was complete, the field was swept back to 100 G and data were obtained on warming the sample (Figure S3). These measurements were repeated approximately 4 days later (91 hours between the two measurements).

6. Activation energy as a function of particle size.

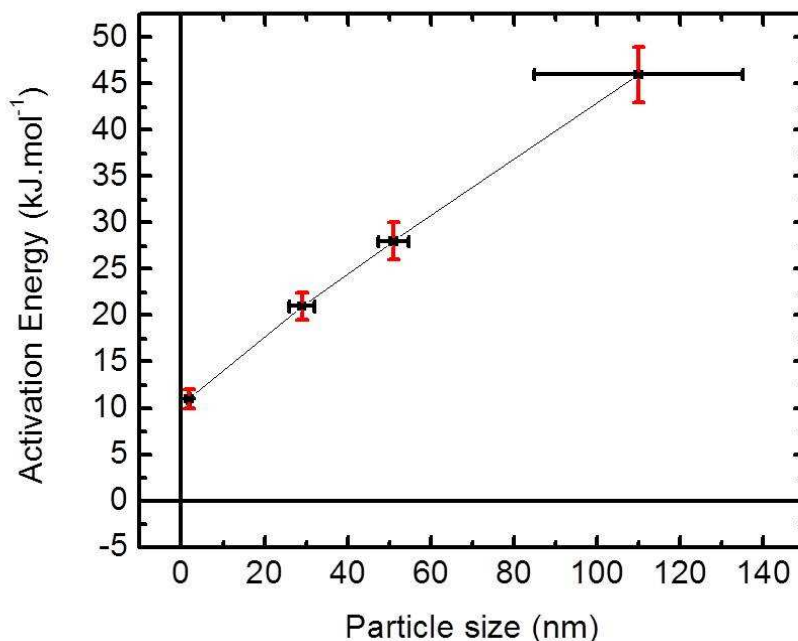


Figure S4. Activation energy as a function of particle size based on the value in Table 1 and section 7 of the Supporting Information. (gray line is a guide for the eyes)

7. Particle size distribution.

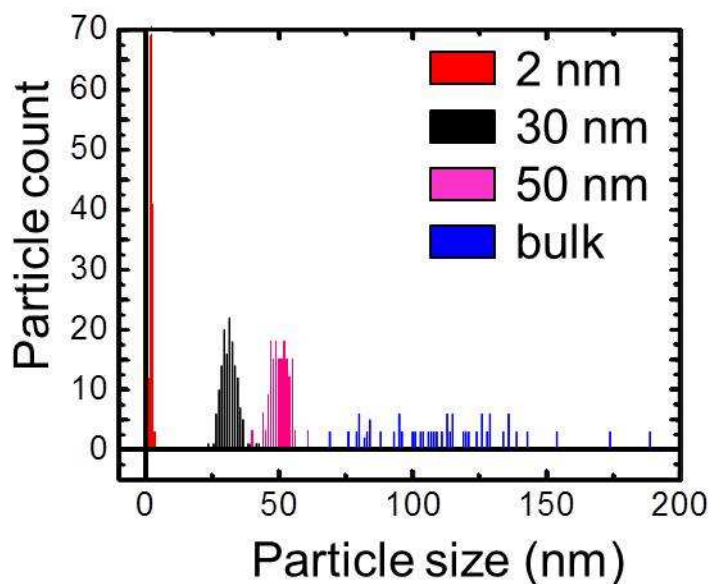


Figure S5. Diagram showing the particle size distribution for each of the samples. red columns represent the 2 nm sample (8) (■), 2 ± 1 nm; black columns represent the 30 nm sample (3) (■), 29 ± 3.1 nm; pink columns represent the 50 nm sample (2) (■), 51 ± 3.6 nm; blue columns represent the bulk sample (1) (■), 110 ± 25 nm;. For each sample >150 particles were measured, taken from pictures of different areas on the TEM grid, using ImageJ software.