Supporting Information

Synthesis of nanocrystals and particle size effects studies on the thermally induced spin transition of the model spin crossover compound $[Fe(phen)_2(NCS)_2]$

Francisco Javier Valverde-Muñoz,[a] Ana B. Gaspar,[a*] Sergii I. Shylin,[b,c] Vadim Ksenofontov,[b] José A. Real[a*]
Corresponding authors: ana.b.gaspar@uv.es, jose.a.real@uv.es

Supporting figures:

Figure S1. Scheme of the synthesis of nanocrystals of compound $[Fe(phen)_2(NCS)_2]$.

Figure S2. SEM photographs illustrating the crystal defects in samples **1*** and **2***.

Figure S3. Powder x-ray diffraction patterns of $[Fe(phen)_2(NCS)_2]$ at 293 K: calculated from the crystal structure[33d] and the nanocrystals **1-6** (experimental).

Figure S4. IR spectra recorded at 293 K for **1-6, 1*** and **2*** (a) and for sodium bis-(2-ethylhexyl) sulfosuccinate (NaOT) (b).

Figure S5. Mössbauer spectra of a reproduction of nanocrystals **1,** synthesis **1***, measured at 293 and 84 K (blue: LS doublet; red: HS doublet). ($\delta_{,HS}$): 0.985(5) mms^{-1}; ($\Delta E_{Q,HS}$): 2.650(1) mms^{-1}. ($\delta_{,LS}$): 0.463(3) mms^{-1}; ($\Delta E_{Q,LS}$): 0.360(5) mms^{-1}. At 293 K, the population of Fe(II) centers in the HS state is 100% whereas at 84 K 100% of the Fe(II) centers are in the LS state.

Figure S6. Comparison of the crystallite's size obtained from SEM measurements and from Scherrer equation for samples **1-6**.

Supporting tables:

Table S1. Series of additional experiments performed in the synthesis of nanocrystals of compound $[Fe(phen)_2(NCS)_2]$ applying the reverse micelle method (a) and using PVP as coating polymer (b).

Table S2. Images used for particle size determination and the resultant statistics for the samples **1-6**. w = $[H_2O]$+[MeOH]/[NaOT], c = [Fe(II)] (M), Dim = dimensions $(nm)^3$, L = length (nm), W = width (nm), StdDev = standard deviation (nm) and population (count). The dimensions L and W of the nanocrystals are calculated as the arithmetic average of three independent measurements using different SEM images.

Table S3. Summary on crystallite sizes for **1-6** obtained from Scherrer's equation using the reflections (002), (110), (111) and (023).

Figure S1. Scheme of the synthesis of nanocrystals of compound $[Fe(phen)_2(NCS)_2]$.

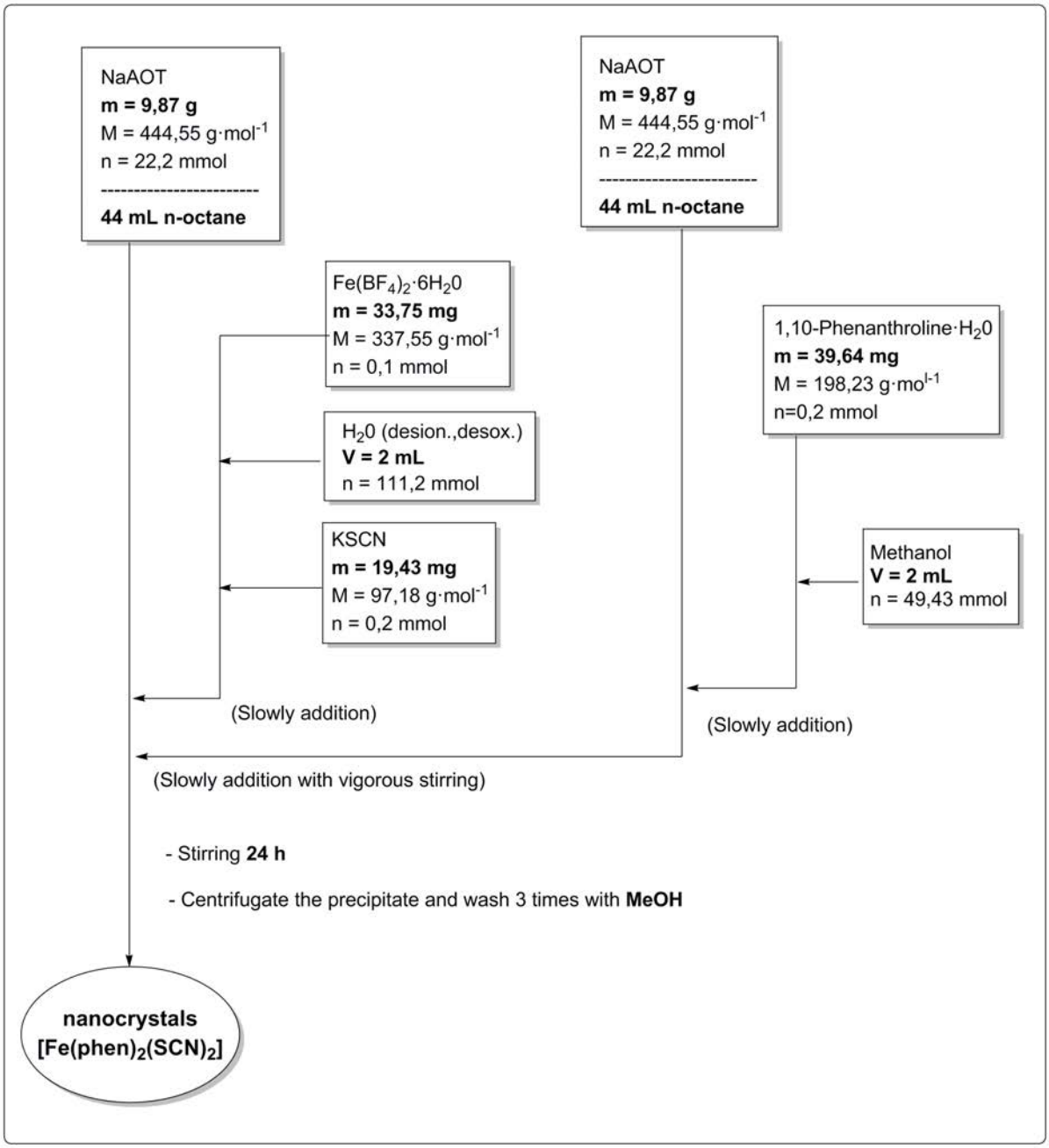
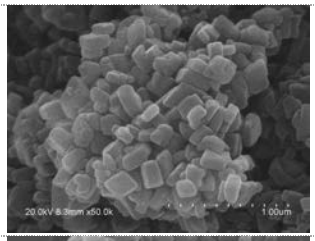
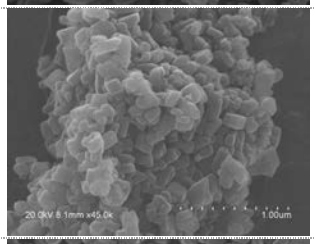
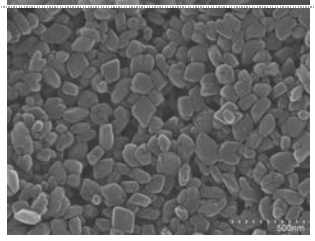
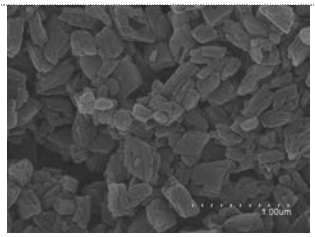
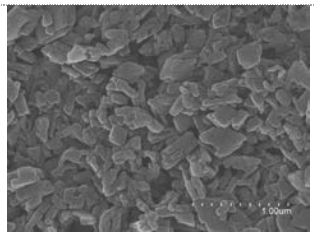
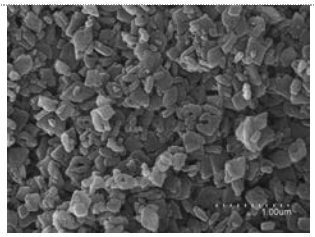
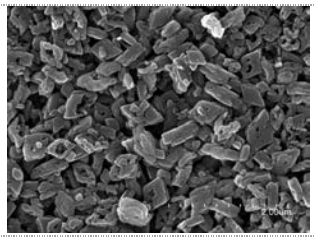
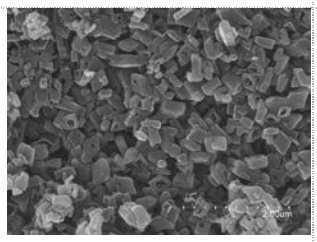


Table S1. Series of additional experiments performed in the synthesis of nanocrystals of compound $[Fe(phen)_2(NCS)_2]$ applying the reverse micelle method (a) and using PVP as coating polymer (b).

(a) Reverse micelle method						
Sample code	**[Fe(II)] mmol**	**ϖ = [solvent]/ [NaOT]**	**Reaction time (h)**	**Temperature (K)**	**Result**	**Comments on crystal growth and morphology**
a	0.05	3.6	24	293	Particles of compound $[Fe(phen)_2(NCS)_2]$ didn't form, instead a red solution of compound $\{[Fe(phen)_3](NCS)_2\}$ was isolated.	---
b	0.05	3.6	168	293	Particles of compound $[Fe(phen)_2(NCS)_2]$ didn't form, instead a red solution of compound $\{[Fe(phen)_3](NCS)_2\}$ was isolated.	---
c	0.1	3.6	16	293		Rhombohedric
d	0.1	3.6	18	293		Rhombohedric
e	0.1	3.6	6	273		The morphology of the crystals approaches the rhombohedric, however, from the images is clearly seen that the majority of the crystals were still growing when the synthesis was stopped.
f	0.1	2	24	293	Particles of compound $[Fe(phen)_2(NCS)_2]$ didn't form, instead a red solution of compound $\{[Fe(phen)_3](NCS)_2\}$ was isolated.	----

g	0.1	5	1	293		Very low yield; only 1mg of particles was isolated and from the images one can infer that the crystallization process wasn't finish.
h	0.1	5	2	293		Very low yield; nearly 1mg of particles was isolated and from the images one can infer that the crystallization process wasn't finish.
i	0.1	5	4	293		Very low yield; around 1mg of particles was isolated and from the images one can infer that the crystallization process wasn't finish.
j	0.1	5	24	293		Bad crystals, the crystallization process weren't finish; low yield only 10 mg of particles was isolated.
k	0.15	5	24	293	Particles of compound $[Fe(phen)_2(NCS)_2]$ didn't form, instead a red solution of compound $\{[Fe(phen)_3](NCS)_2\}$ was isolated	---
l	0.2	5	24	293		Poorly formed crystals but high yield; around 60 mg of particles were isolated.

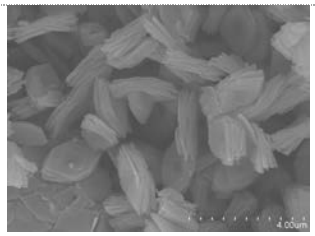
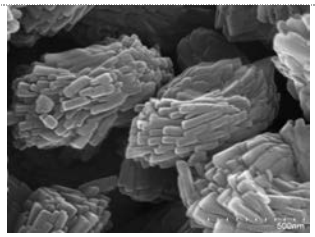
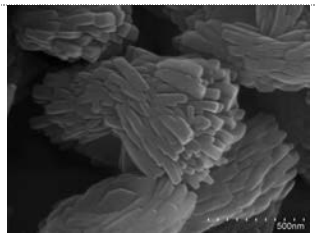
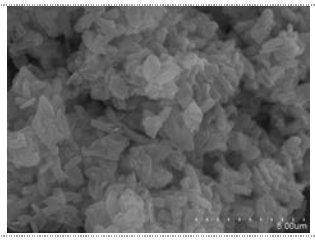
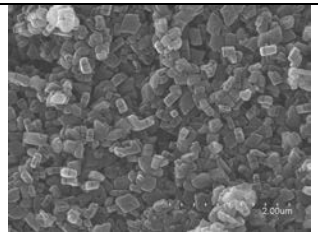
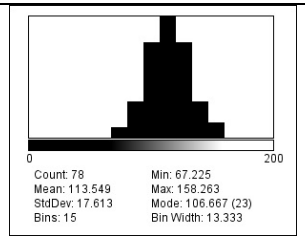
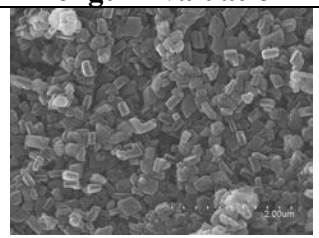
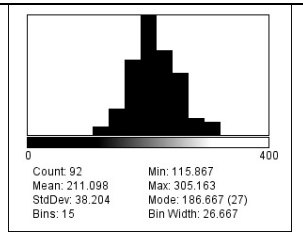
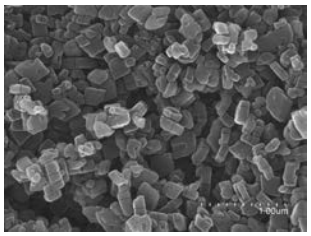
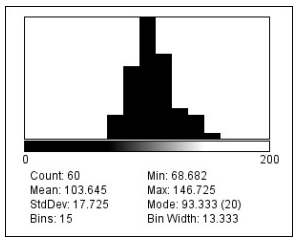
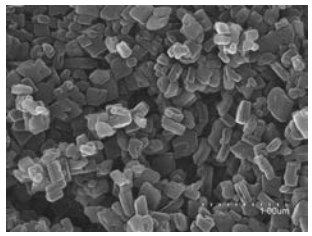
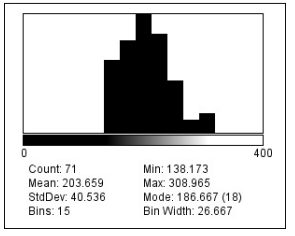
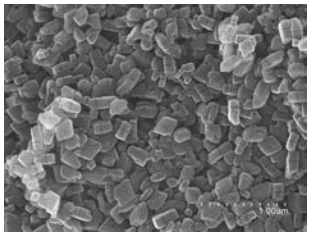
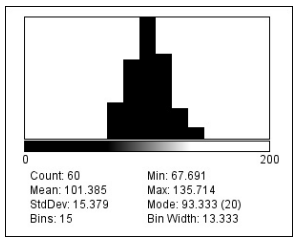
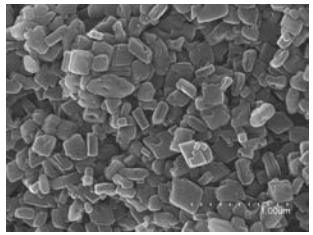
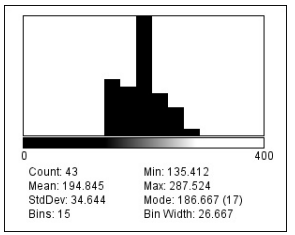
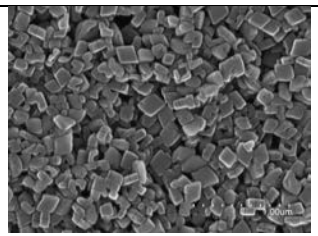
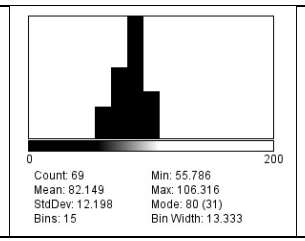
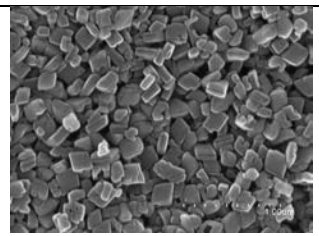
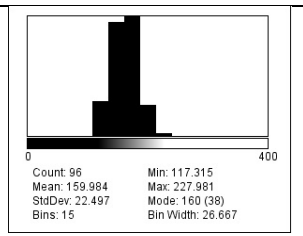
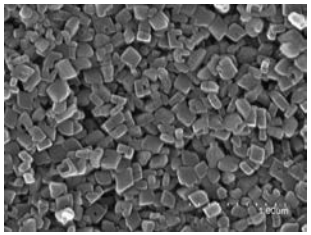
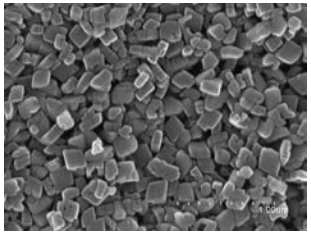
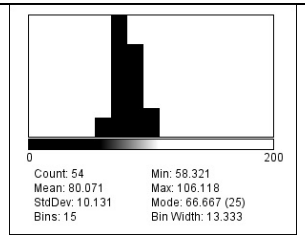
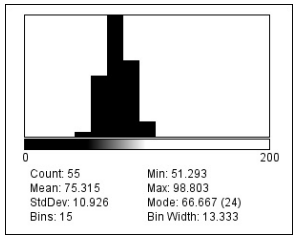
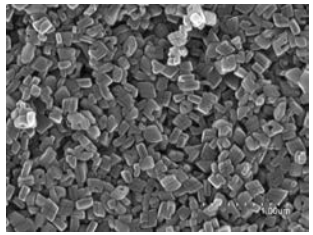
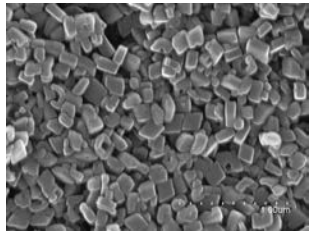
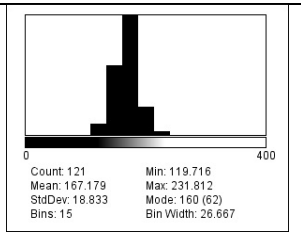
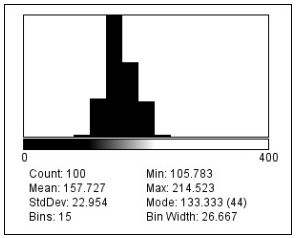
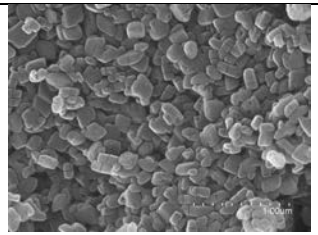
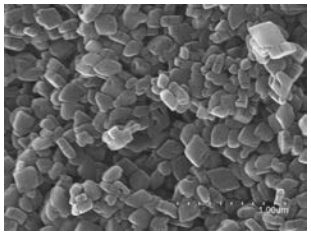
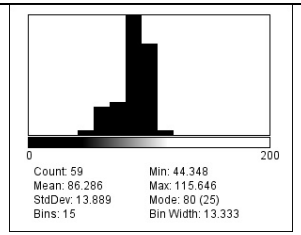
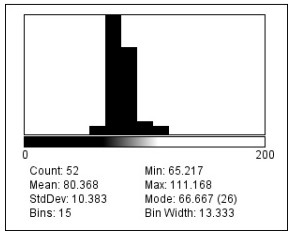
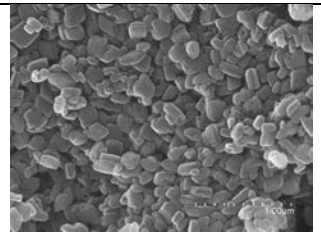
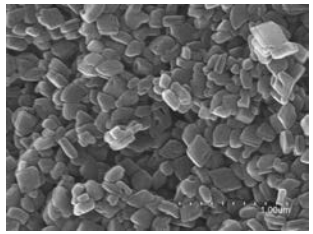
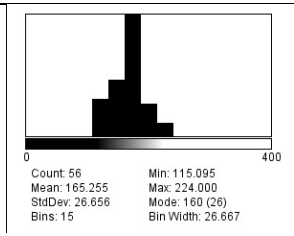
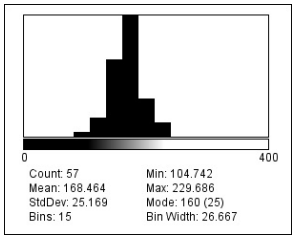
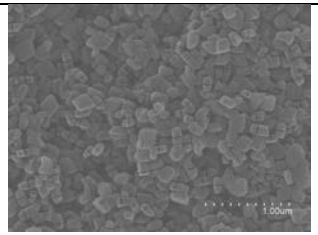
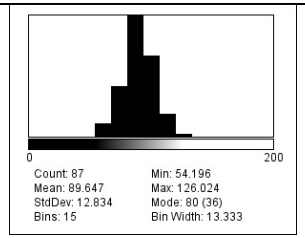
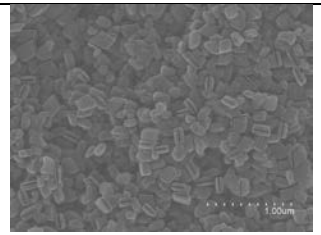
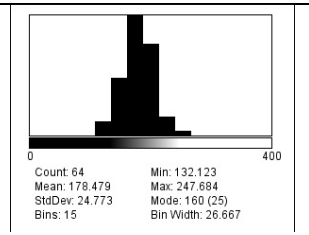
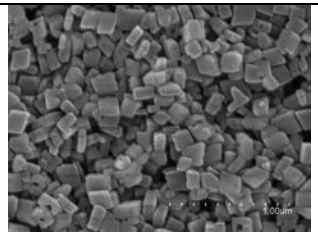
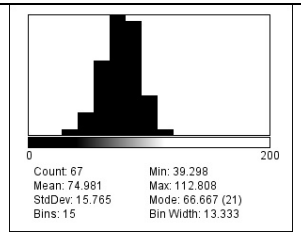
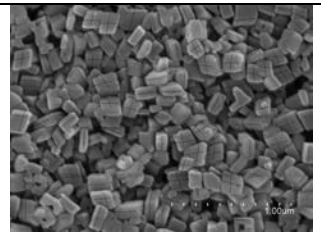
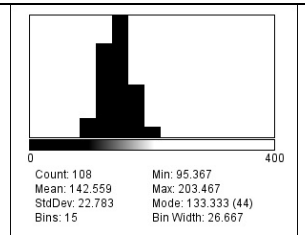
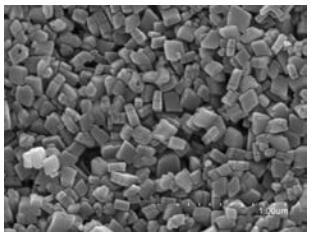
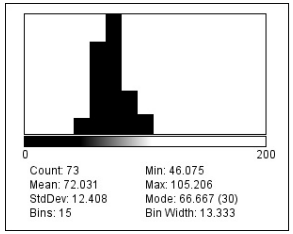
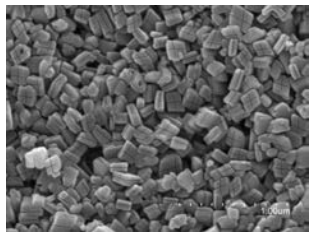
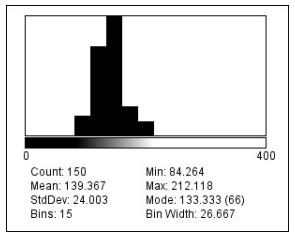
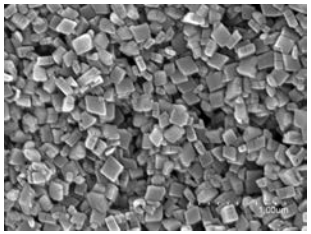
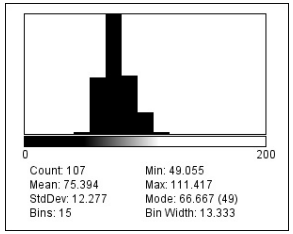
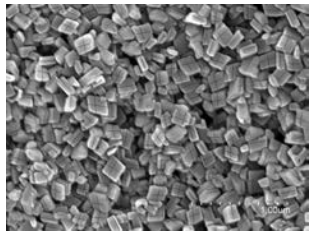
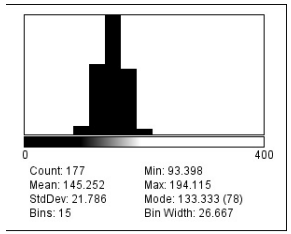
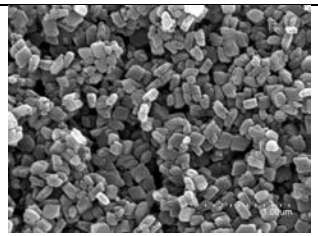
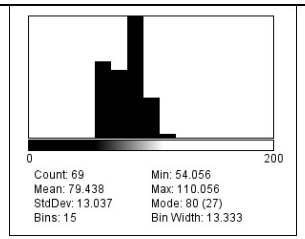
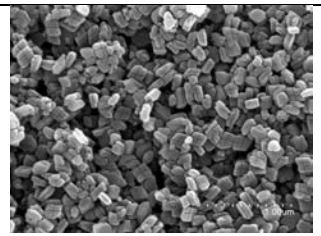
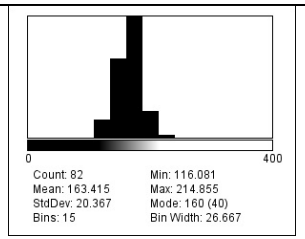
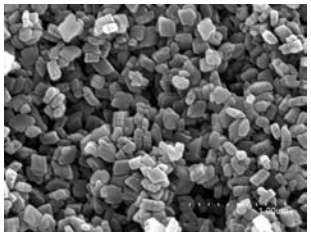
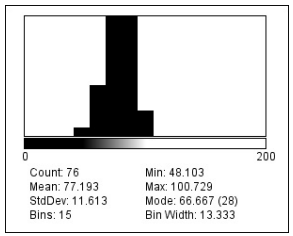
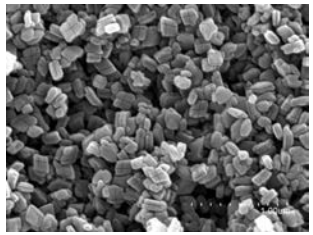
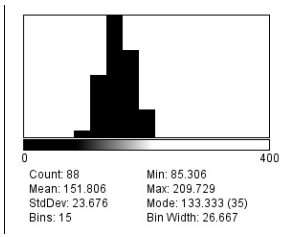
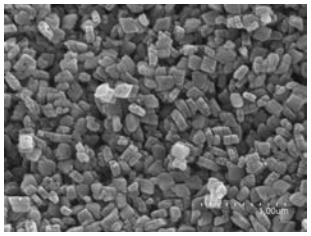
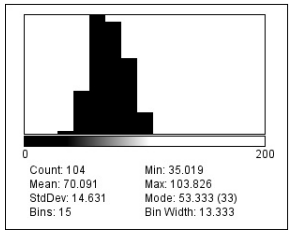
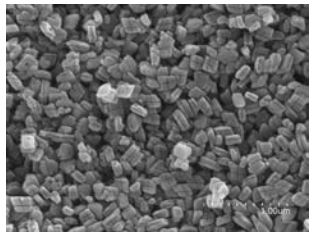
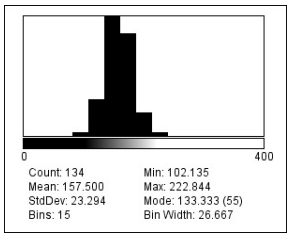
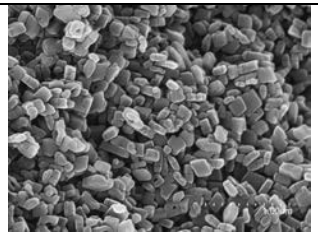
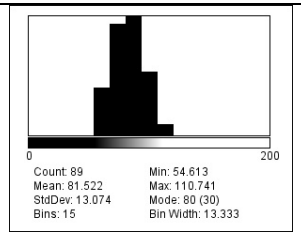
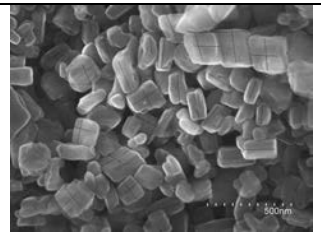
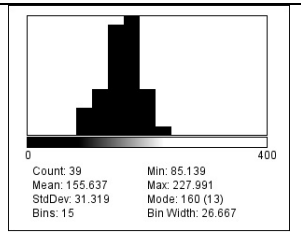
(b) PVP polymer						
Sample code	**[Fe(II)] mmol**	**ϖ = [solvent]/ [PVP]**	**Reaction time (h)**	**Temperature (K)**	**Result**	**Comments on crystal growth and morphology**
a'	0.05	24	24	293	Particles of compound $[Fe(phen)_2(NCS)_2]$ didn't form, instead a red solution of compound $\{[Fe(phen)_3](NCS)_2\}$ was isolated.	------
b'	0.1	24	24	293		Agglomerate of hexagonal platelets of micron dimensions in length and hundred nanometers in width.
c'	0.1	24	24	293		Agglomerate of prismatic platelets of micron dimensions in length and hundred nanometers in width.
d'	0.1	6	6	293		Agglomerate of prismatic platelets of micron dimensions in length and hundred nanometers in width.
e'	0.2	24	24	293		Agglomerate of microparticles with no well defined morphology.

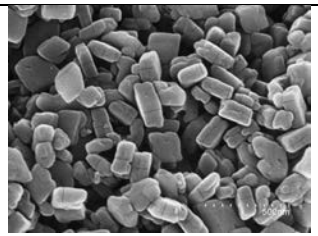
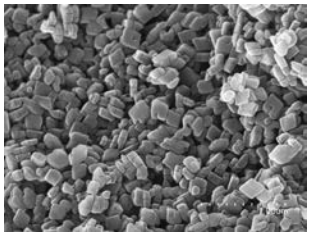
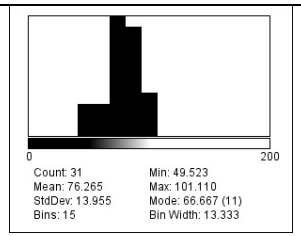
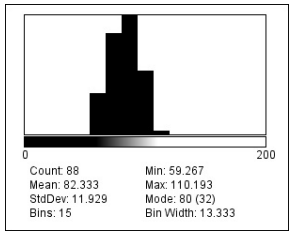
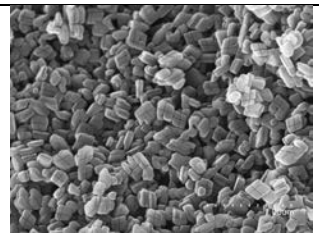
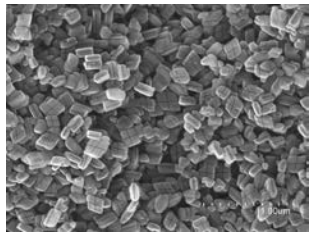
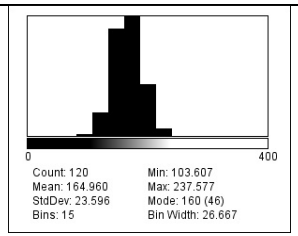
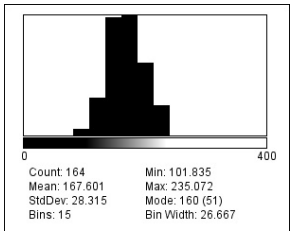
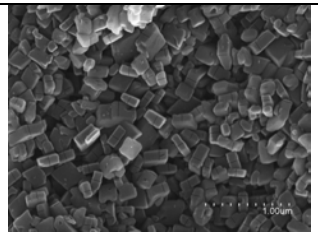
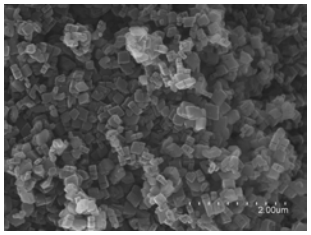
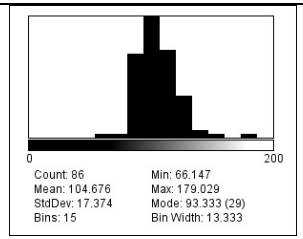
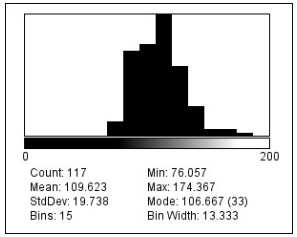
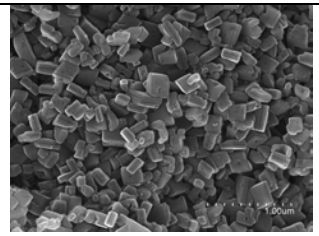
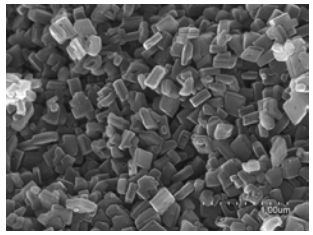
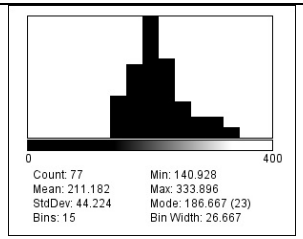
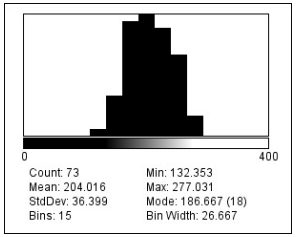
Table S2. Images used for particle size determination and the resultant statistics for the samples **1-6**. w = [H_2O]+[MeOH]/[NaOT], c = [Fe(II)] (M), Dim = dimensions $(nm)^3$, L = length (nm), W = width (nm), StdDev = standard deviation (nm) and population (count). The dimensions L and W of the nanocrystals are calculated as the arithmetic average of three independent measurements using different SEM images.

Sample	Dim	Width Evaluation	Statistics	Length Evaluation	Statistics
1	203 x 203 x 106				
		W = 113.549		L = 211.098	
					
		W = 103.645		L = 203.659	
					
		W = 101.385		L = 194.845	
2	162 x 162 x 79				

		W = 82.149  W = 80.071  W = 75.315	 	L = 159.984  L = 167.179  L = 157.727	 
3	171 x171 x 85	 W = 86.286  W = 80.368	 	 L = 165.255  L = 168.464	 

		 W = 89.647		 L = 178.479	
4	142 x142 x 74	 W = 74.981		 L = 142.559	
		 W = 72.031		 L = 139.367	
		 W = 75.394		 L = 145.252	

5	158 x 158 x 76	 W = 79.438		 L = 163.415	
		 W = 77.193		 L = 151.806	
		 W = 70.091		 L = 157.500	
6	163 x 163 x 80	 W = 81.522		 L = 155.637	

		 W = 76.265  W = 82.333	 	 L = 164.960  L = 167.601	 
1*	206x206x106 206±40 106±19	 W = 104.676  W = 109.623	 	 L = 211.182  L = 204.016	 

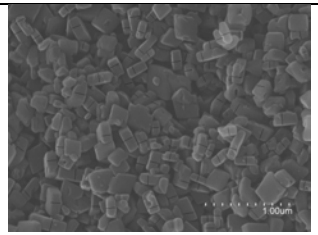
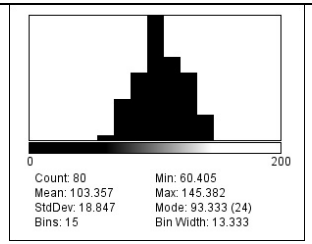
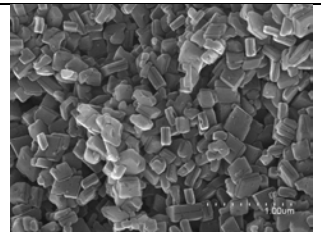
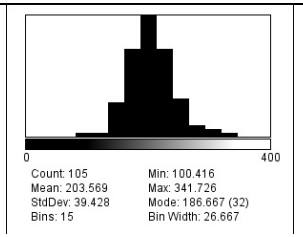
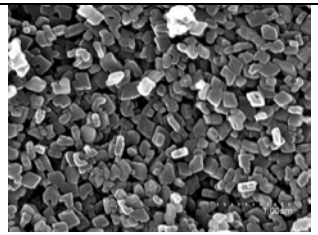
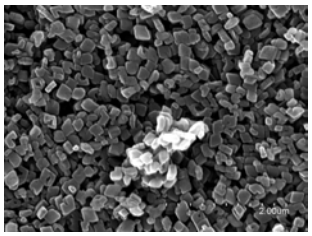
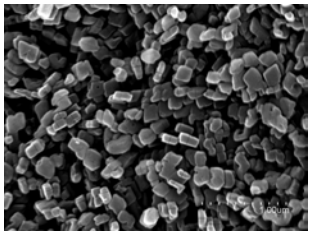
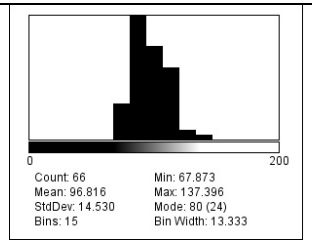
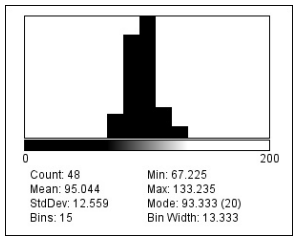
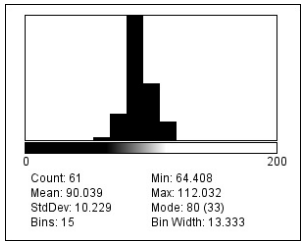
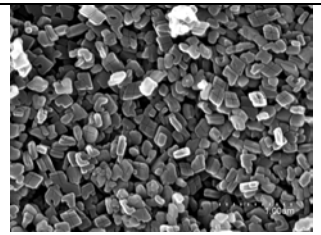
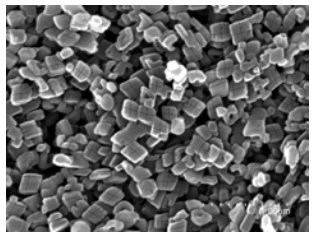
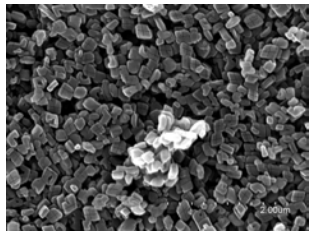
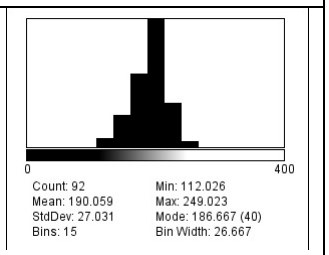
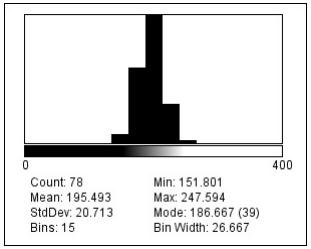
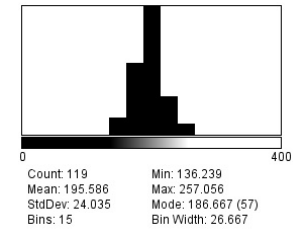
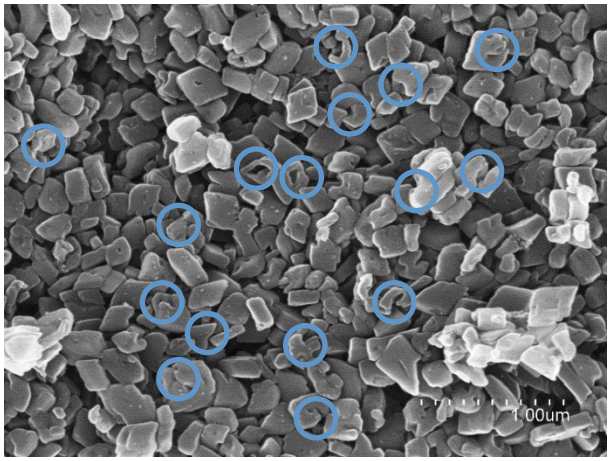
		 W = 103.357		 L = 203.569	
2*	194 x 194 x 94 194±24 94±12	 W = 96.816  W = 95.044  W = 90.039	  	 L = 190.059  L = 195.493  L = 195.586	  

Figure S2. SEM photographs illustrating the crystal defects in samples **1*** and **2***.

1*



2*

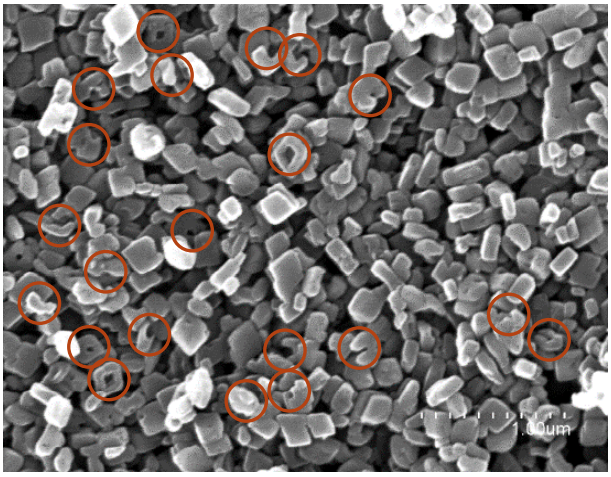


Figure S3. Powder x-ray diffraction patterns of $[Fe(phen)_2(NCS)_2]$ at 293 K: calculated from the crystal structure[33d] and the nanocrystals **1**-**6** (experimental).

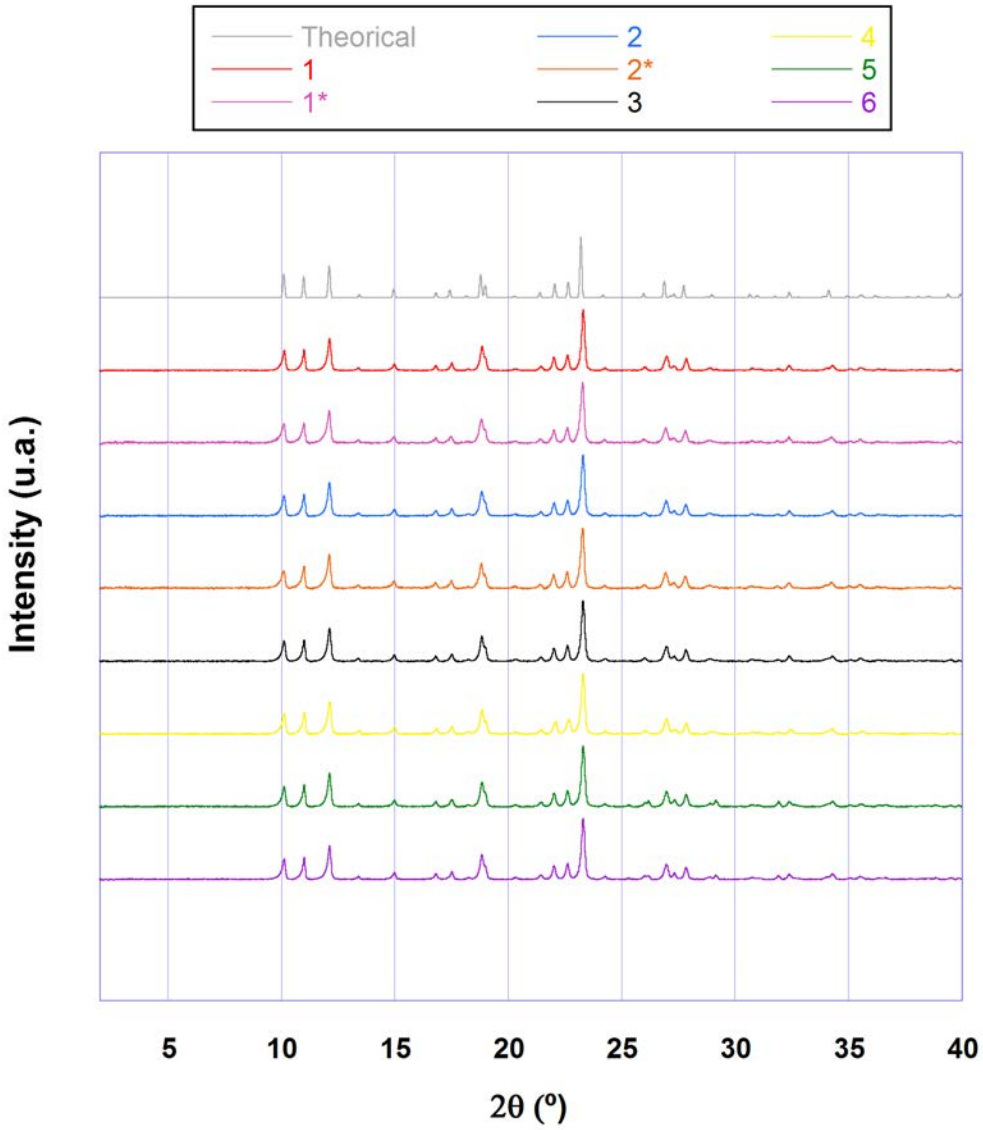
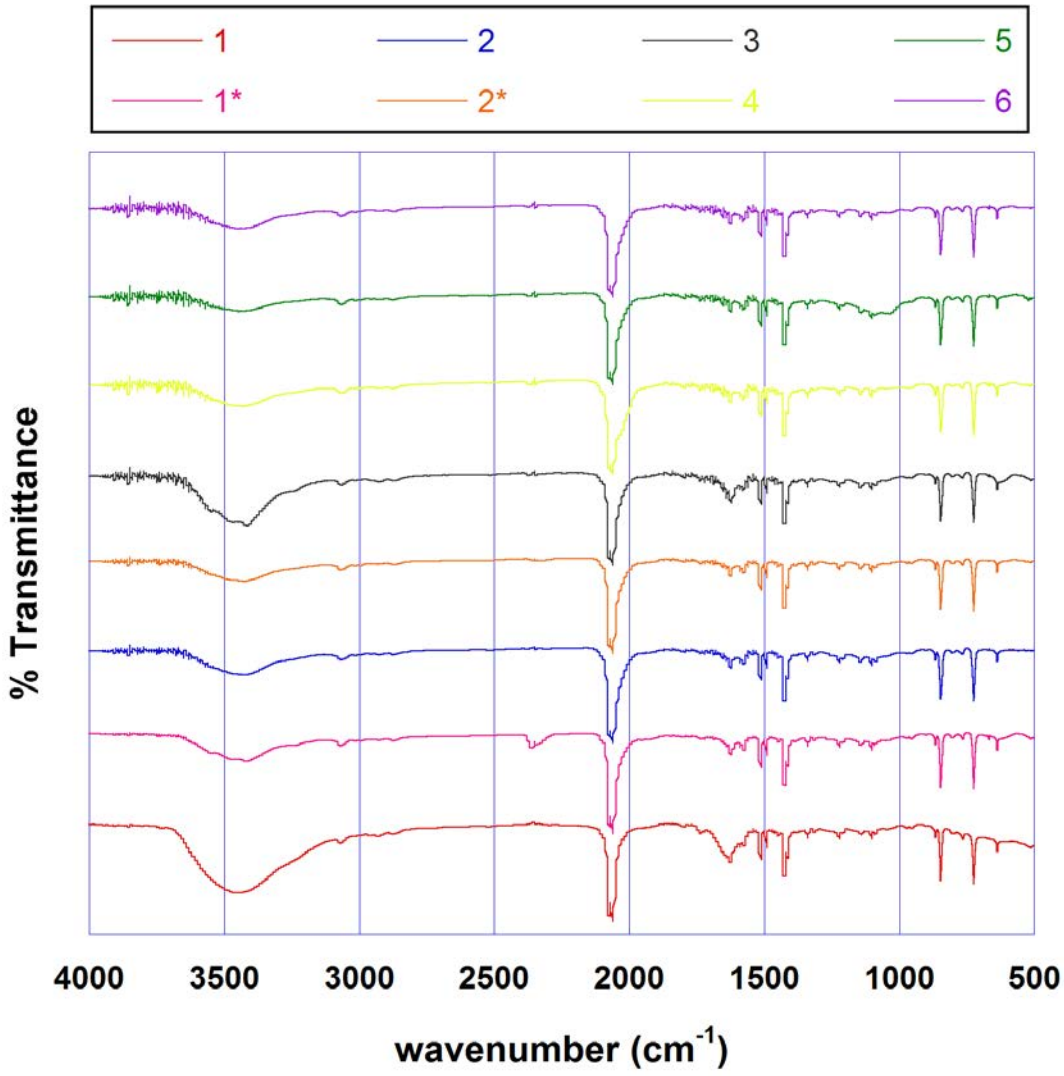


Figure S4. IR spectra recorded at 293 K for **1-6, 1*** and **2*** (a) and for sodium bis-(2-ethylhexyl) sulfosuccinate (NaOT) (b).

(a)



(b)

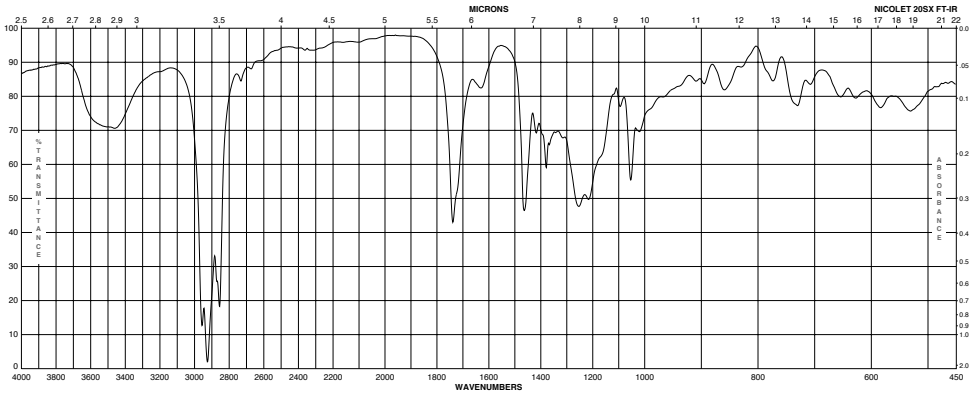


Figure S5. Mössbauer spectra of a reproduction of nanocrystals **1,** synthesis **1***, measured at 293 and 84 K (blue: LS doublet; red: HS doublet). ($\delta_{, HS}$): 0.985(5) mms^{-1}; ($\Delta E_{Q, HS}$): 2.650(1) mms^{-1}. ($\delta_{, LS}$): 0.463(3) mms^{-1}; ($\Delta E_{Q, LS}$): 0.360(5) mms^{-1}. At 293 K, the population of Fe(II) centers in the HS state is 100% whereas at 84 K 100% of the Fe(II) centers are in the LS state. The line width for the HS and LS states is: Γ(HS) = 0.136(9) mm/s and Γ(LS) = 0.141(5) mm/s.

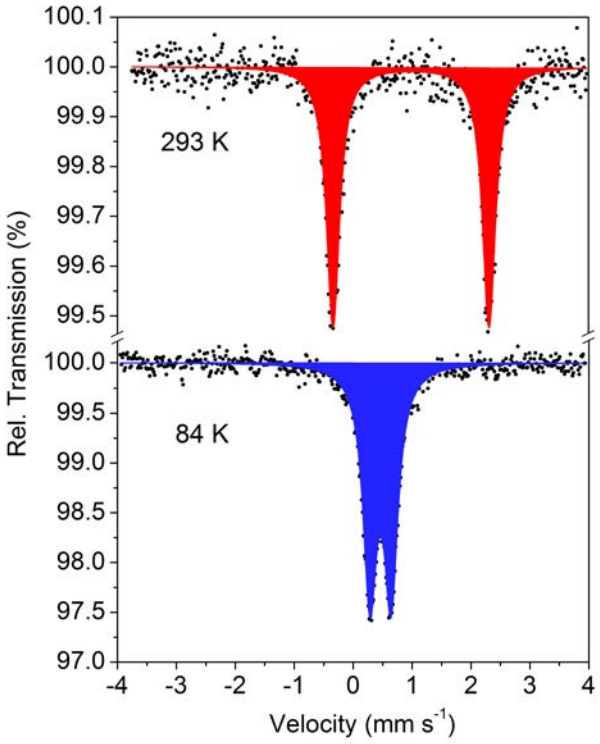


Table S3. Summary on crystallite sizes for **1-6** obtained from Scherrer's equation using the reflections (002), (110), (111) and (023). The parameter K was fixed at the value of 1, the λ_{α} = 1,540598 Å and the standard used to calibrate the instrumental broadening was LaB_6.

References to Scherrer equation :a) P. Scherrer, *Mathematisch-Physikalische Klasse* **1918**, *2*, 98; b) *T. Ungár*, *Adv. Eng. Mat.* **2003**, *5*, 323 .

	sample 1	[Fe^{II}]=0,1 mmol			
Reflexions	**(2θ)**	**B obs. (2θ)**	**B std. (2θ)**	**B strc. (2θ)**	**dimension (nm)**
(002)	10,14	0,1712	0,079	0,0922	96,3
(110)	11,00	0,1412	0,079	0,0622	143
(111)	12,13	0,1801	0,079	0,1011	87,9
(023)	23,31	0,145	0,079	0,066	136,6

	sample 2	[Fe^{II}]=0,15 mmol			
Reflexions	**(2θ)**	**B obs. (2θ)**	**B std. (2θ)**	**B strc. (2θ)**	**dimension (nm)**
(002)	10,12	0,1833	0,079	0,1043	85,2
(110)	11,00	0,1482	0,079	0,0692	128,5
(111)	12,12	0,1832	0,079	0,1042	85,4
(023)	23,3	0,1701	0,079	0,0911	99

	sample 3	[Fe^{II}]=0,2 mmol			
Reflexions	**(2θ)**	**B obs. (2θ)**	**B std. (2θ)**	**B strc. (2θ)**	**dimension (nm)**
(002)	10,12	0,1873	0,079	0,1083	82,1
(110)	11,02	0,1482	0,079	0,0692	128,5
(111)	12,12	0,1702	0,079	0,0912	97,5
(023)	23,3	0,1661	0,079	0,0871	103,6

	sample 4	[Fe^{II}]=0,3 mmol			
Reflexions	**(2θ)**	**B obs. (2θ)**	**B std. (2θ)**	**B strc. (2θ)**	**dimension (nm)**
(002)	10,13	0,1903	0,079	0,1113	79,8
(110)	11,02	0,1472	0,079	0,0682	130,4
(111)	12,13	0,1952	0,079	0,1162	76,5
(023)	23,3	0,1711	0,079	0,0921	98

	sample 5	[Fe^{II}]=0,4 mmol			
Reflexions	**(2θ)**	**B obs. (2θ)**	**B std. (2θ)**	**B strc. (2θ)**	**dimension (nm)**
(002)	10,13	0,1943	0,079	0,1153	77,1
(110)	11,02	0,1472	0,079	0,0682	130,4
(111)	12,12	0,1752	0,079	0,0962	92,5
(023)	23,3	0,1521	0,079	0,0731	123,5

	sample 6	[Fe^{II}]=0,5 mmol			
Reflexions	**(2θ)**	**B obs. (2θ)**	**B std. (2θ)**	**B strc. (2θ)**	**dimension (nm)**
(002)	10,13	0,1703	0,079	0,0913	97,4
(110)	11,02	0,1392	0,079	0,0602	147,8
(111)	12,13	0,1761	0,079	0,0971	91,5
(023)	23,3	0,15	0,079	0,071	126,9

Figure S6. Comparison of the crystallite's size obtained from SEM measurements and from Scherrer equation for samples **1**-**6**.