

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]

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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). (δ_{HS}): 0.985(5) mms⁻¹; ($\Delta E_{\text{Q, HS}}$): 2.650(1) mms⁻¹. (δ_{LS}): 0.463(3) mms⁻¹; ($\Delta E_{\text{Q, LS}}$): 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**. $w = [\text{H}_2\text{O}] + [\text{MeOH}] / [\text{NaOT}]$, $c = [\text{Fe(II)}]$ (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 $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$.

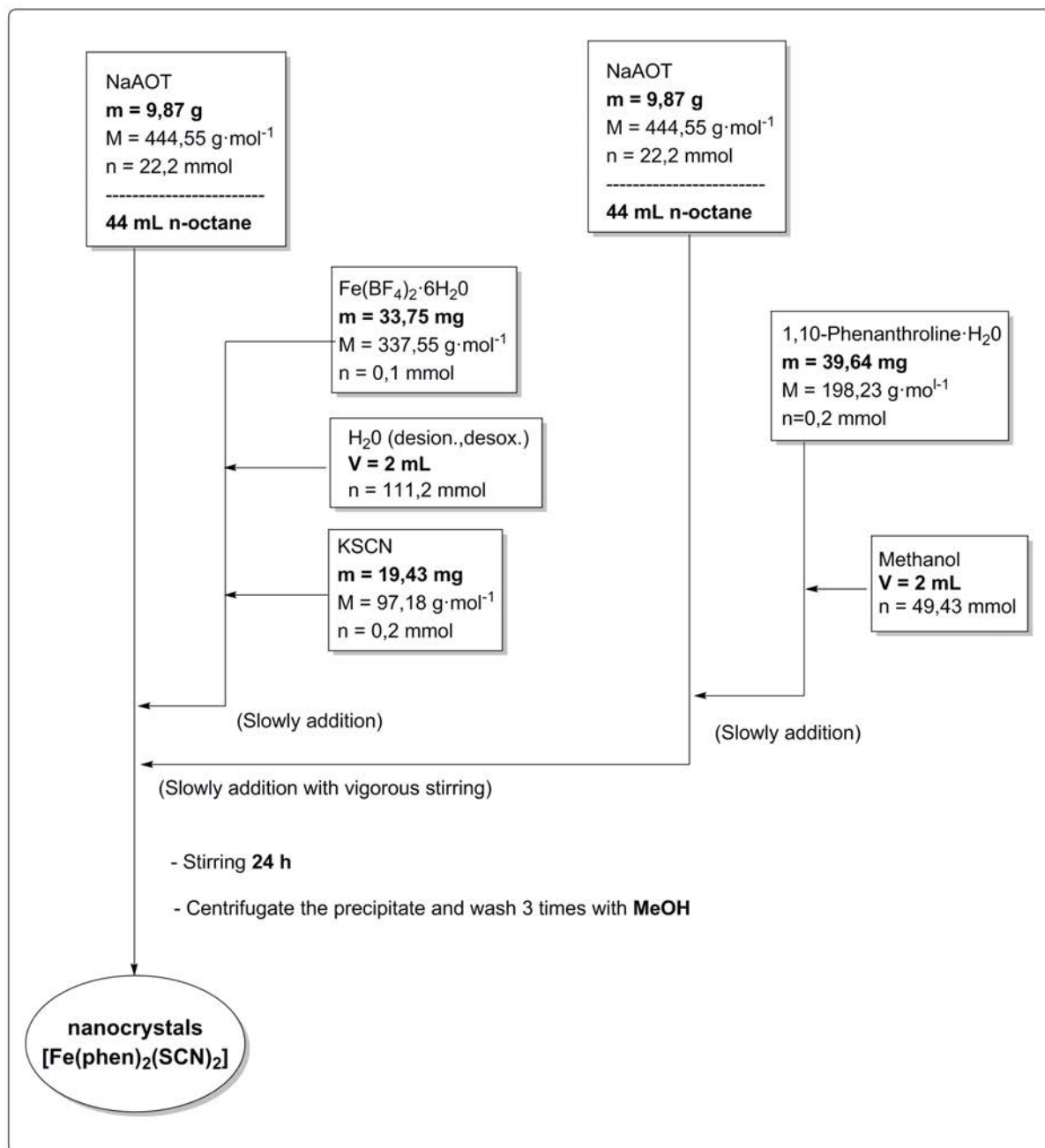
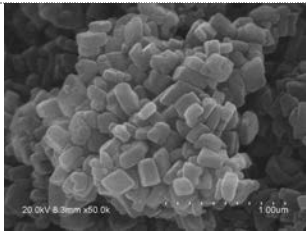
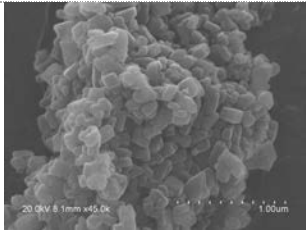
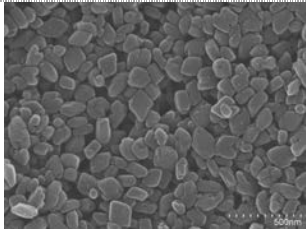
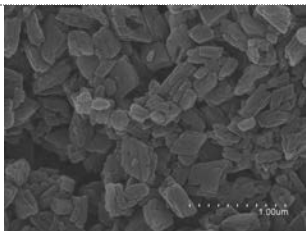
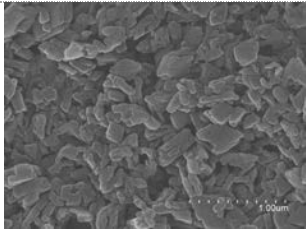
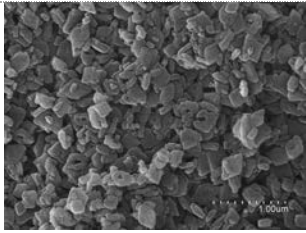
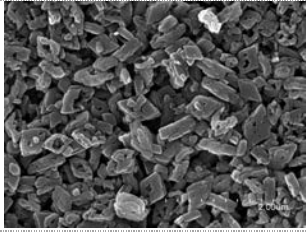
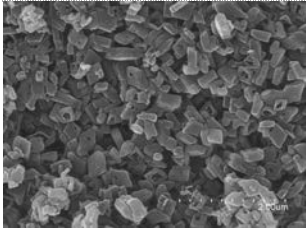


Table S1. Series of additional experiments performed in the synthesis of nanocrystals of compound $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ applying the reverse micelle method (a) and using PVP as coating polymer (b).

(a) Reverse micelle method						
Sample code	[Fe(II)] mmol	$\varpi = \frac{[\text{solvent}]}{[\text{NaOT}]}$	Reaction time (h)	Temperature (K)	Result	Comments on crystal growth and morphology
a	0.05	3.6	24	293	Particles of compound $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ didn't form, instead a red solution of compound $\{[\text{Fe}(\text{phen})_3](\text{NCS})_2\}$ was isolated.	---
b	0.05	3.6	168	293	Particles of compound $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ didn't form, instead a red solution of compound $\{[\text{Fe}(\text{phen})_3](\text{NCS})_2\}$ was isolated.	---
c	0.1	3.6	16	293		Rhombohedral
d	0.1	3.6	18	293		Rhombohedral
e	0.1	3.6	6	273		The morphology of the crystals approaches the rhombohedral, 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 $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ didn't form, instead a red solution of compound $\{[\text{Fe}(\text{phen})_3](\text{NCS})_2\}$ 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 $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ didn't form, instead a red solution of compound $\{[\text{Fe}(\text{phen})_3](\text{NCS})_2\}$ was isolated	
l	0.2	5	24	293		Poorly formed crystals but high yield; around 60 mg of particles were isolated.

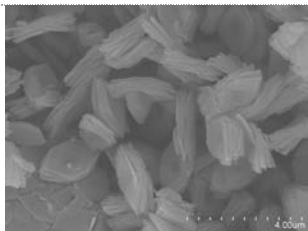
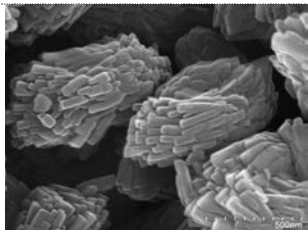
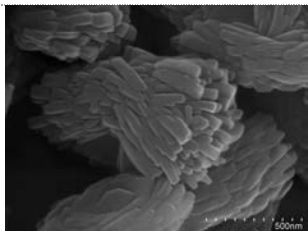
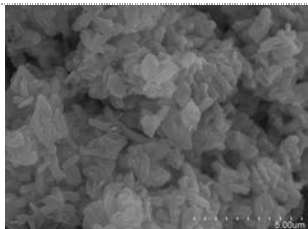
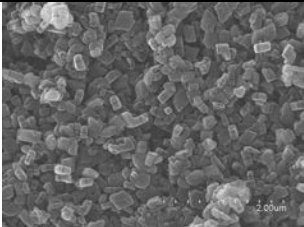
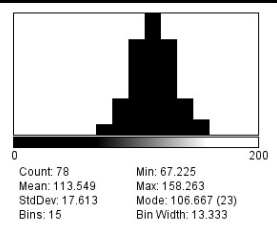
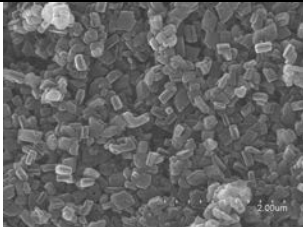
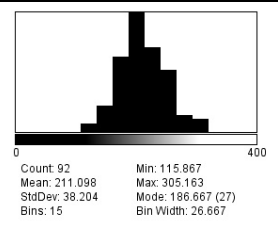
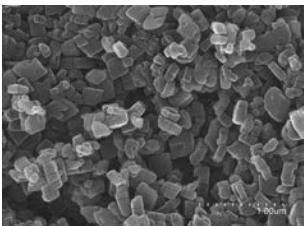
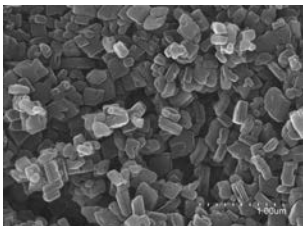
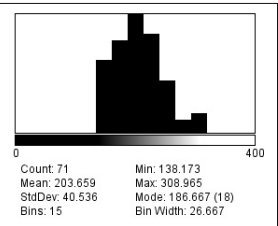
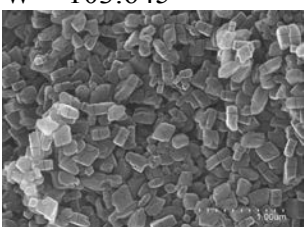
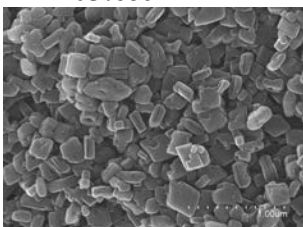
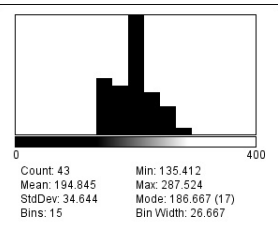
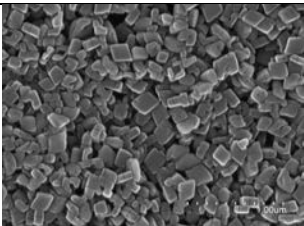
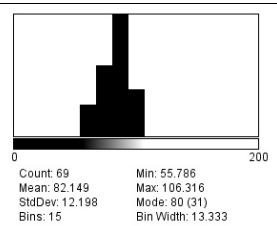
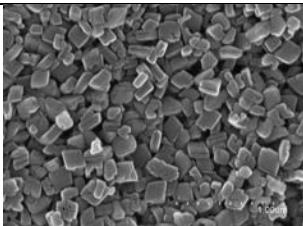
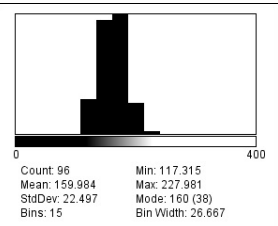
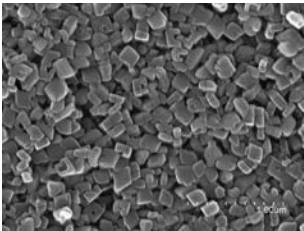
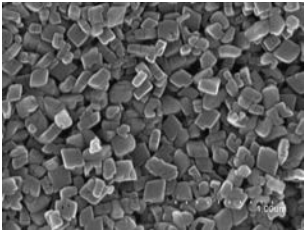
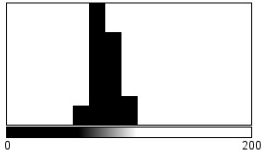
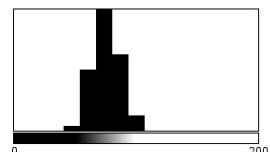
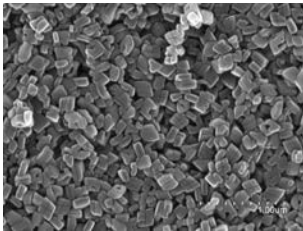
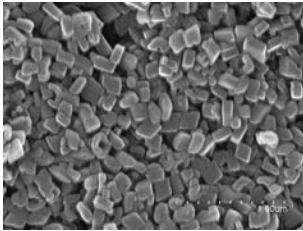
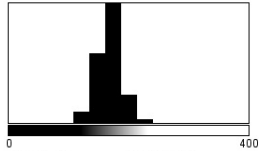
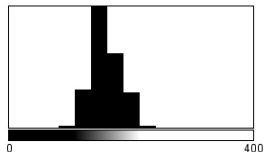
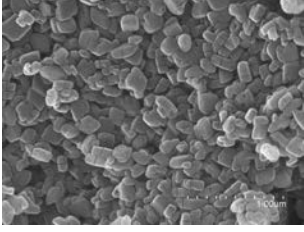
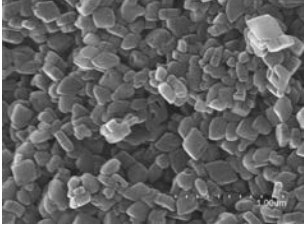
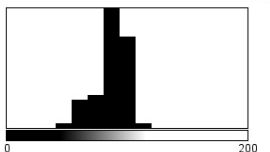
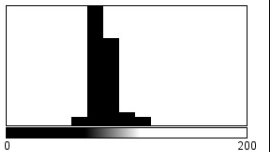
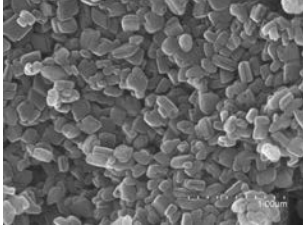
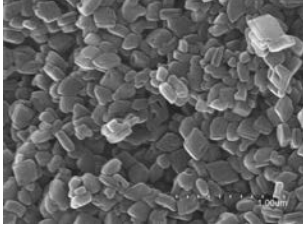
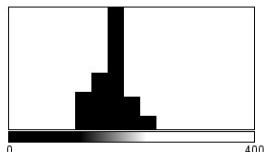
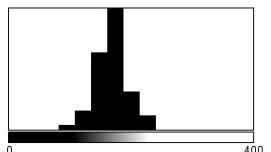
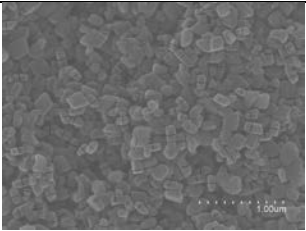
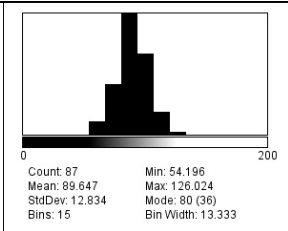
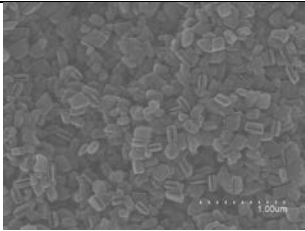
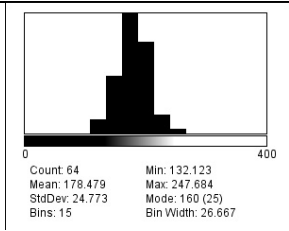
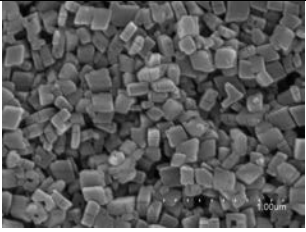
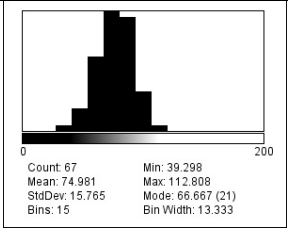
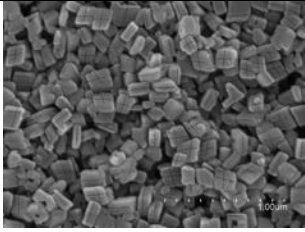
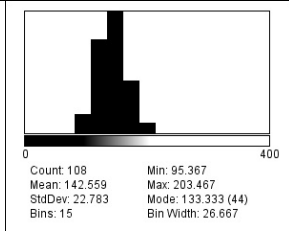
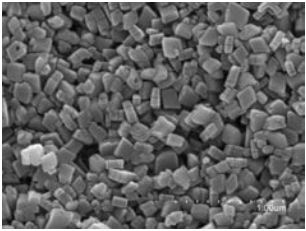
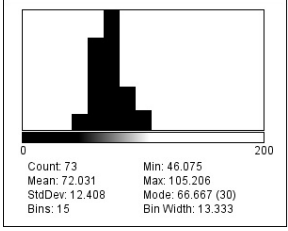
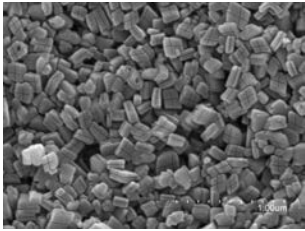
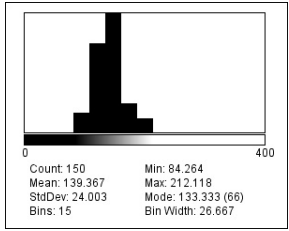
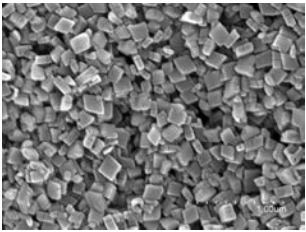
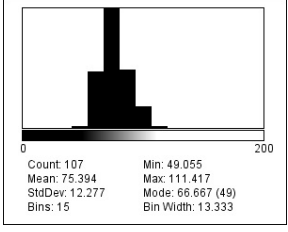
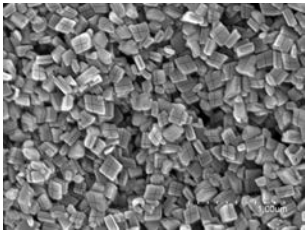
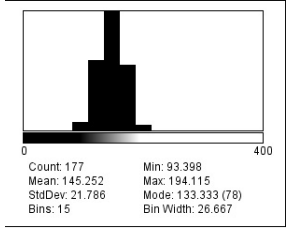
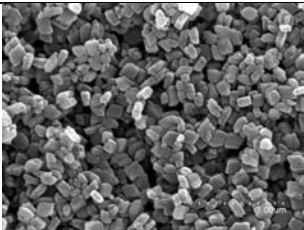
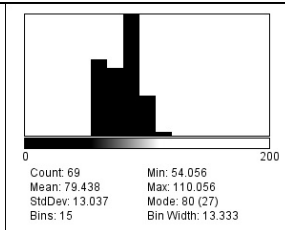
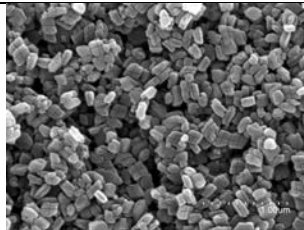
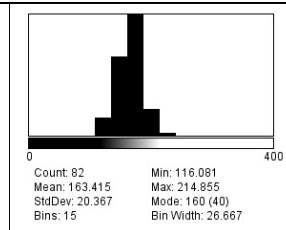
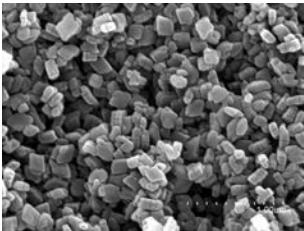
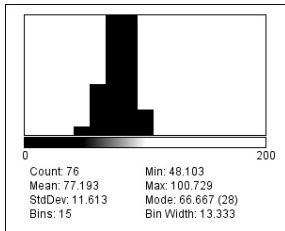
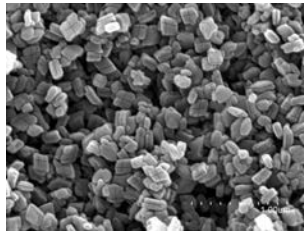
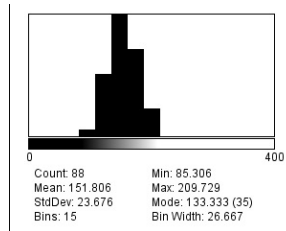
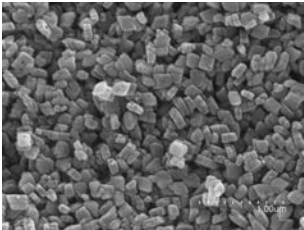
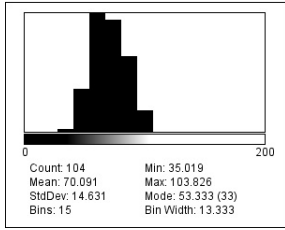
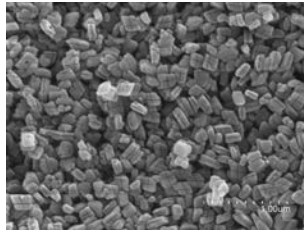
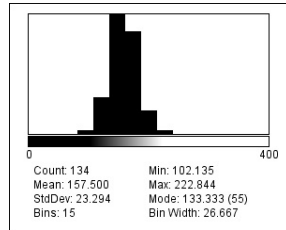
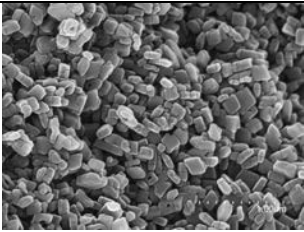
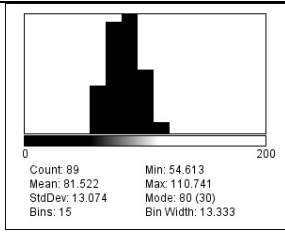
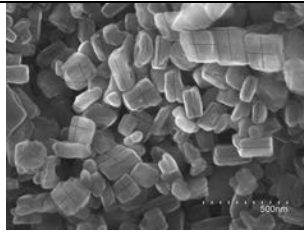
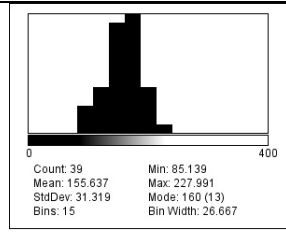
(b) PVP polymer						
Sample code	[Fe(II)] mmol	$\varpi = \frac{[\text{solvent}]}{[\text{PVP}]}$	Reaction time (h)	Temperature (K)	Result	Comments on crystal growth and morphology
a'	0.05	24	24	293	Particles of compound $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ didn't form, instead a red solution of compound $\{[\text{Fe}(\text{phen})_3](\text{NCS})_2\}$ 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.

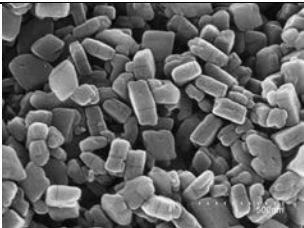
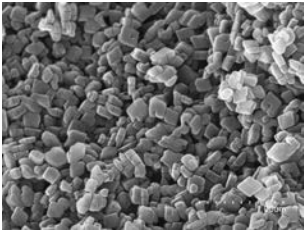
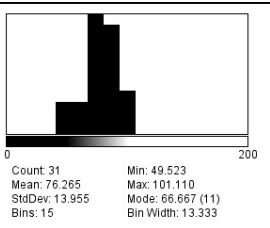
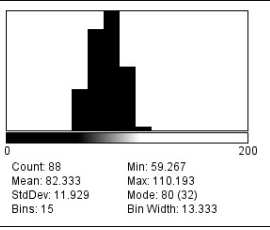
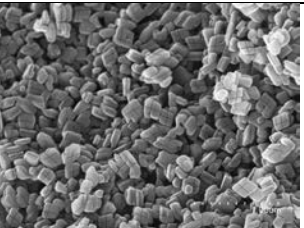
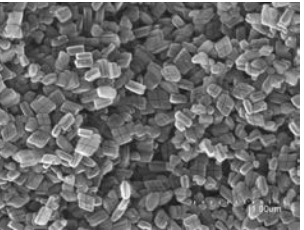
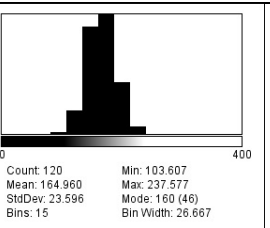
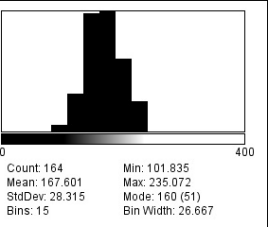
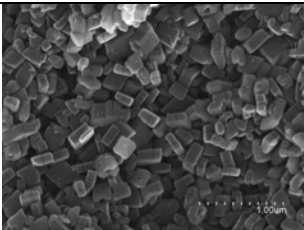
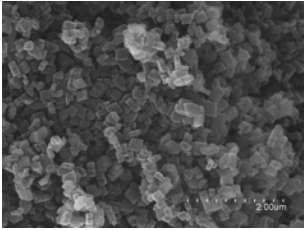
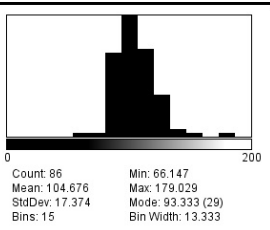
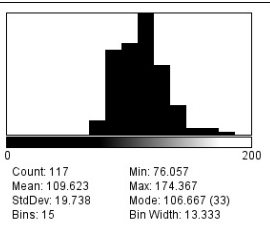
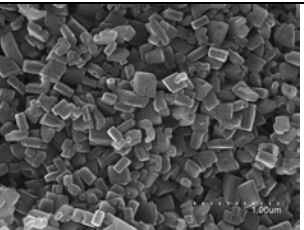
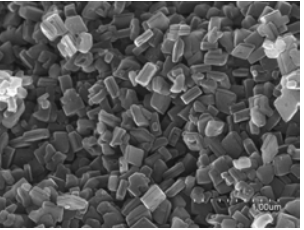
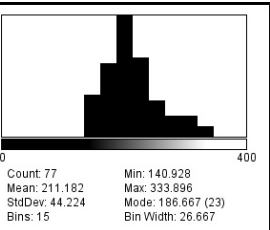
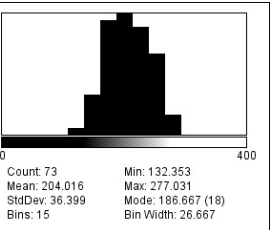
Table S2. Images used for particle size determination and the resultant statistics for the samples **1-6**. $w = [\text{H}_2\text{O}]/[\text{MeOH}]/[\text{NaOT}]$, $c = [\text{Fe(II)}]$ (M), Dim = dimensions (nm)³, L = length (nm), W = width (nm), StdDev = standard deviation (nm) and population (count). 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		 Count: 78 Mean: 113.549 StdDev: 17.613 Bins: 15 Min: 67.225 Max: 158.263 Mode: 106.667 (23) Bin Width: 13.333		 Count: 92 Mean: 211.098 StdDev: 38.204 Bins: 15 Min: 115.867 Max: 305.163 Mode: 186.667 (27) Bin Width: 26.667
		W = 113.549			 Count: 71 Mean: 203.659 StdDev: 40.536 Bins: 15 Min: 138.173 Max: 308.965 Mode: 186.667 (18) Bin Width: 26.667
		W = 103.645			 Count: 43 Mean: 194.845 StdDev: 34.644 Bins: 15 Min: 135.412 Max: 287.524 Mode: 186.667 (17) Bin Width: 26.667
		W = 101.385		L = 194.845	
2	162 x 162 x 79		 Count: 69 Mean: 82.149 StdDev: 12.198 Bins: 15 Min: 55.786 Max: 106.316 Mode: 80 (31) Bin Width: 13.333		 Count: 96 Mean: 159.984 StdDev: 22.497 Bins: 15 Min: 117.315 Max: 227.991 Mode: 160 (38) Bin Width: 26.667

		W = 82.149  W = 80.071  W = 75.315	 Count: 54 Mean: 80.071 StdDev: 10.131 Bins: 15 Min: 58.321 Max: 106.118 Mode: 66.667 (25) Bin Width: 13.333  Count: 55 Mean: 75.315 StdDev: 10.926 Bins: 15 Min: 51.293 Max: 98.803 Mode: 66.667 (24) Bin Width: 13.333	L = 159.984  L = 167.179  L = 157.727	 Count: 121 Mean: 167.179 StdDev: 18.833 Bins: 15 Min: 119.716 Max: 231.812 Mode: 160 (62) Bin Width: 26.667  Count: 100 Mean: 157.727 StdDev: 22.954 Bins: 15 Min: 105.783 Max: 214.523 Mode: 133.333 (44) Bin Width: 26.667
3	171 x171 x 85	 W = 86.286  W = 80.368	 Count: 59 Mean: 86.286 StdDev: 13.889 Bins: 15 Min: 44.348 Max: 115.646 Mode: 80 (25) Bin Width: 13.333  Count: 52 Mean: 80.368 StdDev: 10.383 Bins: 15 Min: 65.217 Max: 111.168 Mode: 66.667 (26) Bin Width: 13.333	 L = 165.255  L = 168.464	 Count: 56 Mean: 165.255 StdDev: 26.656 Bins: 15 Min: 115.095 Max: 224.000 Mode: 160 (26) Bin Width: 26.667  Count: 57 Mean: 168.464 StdDev: 25.169 Bins: 15 Min: 104.742 Max: 229.686 Mode: 160 (25) Bin Width: 26.667

		 W = 89.647	 Count: 87 Min: 54.196 Mean: 89.647 Max: 126.024 StdDev: 12.834 Mode: 80 (36) Bins: 15 Bin Width: 13.333	 L = 178.479	 Count: 64 Min: 132.123 Mean: 178.479 Max: 247.684 StdDev: 24.773 Mode: 160 (25) Bins: 15 Bin Width: 26.667
4	142 x142 x 74	 W = 74.981	 Count: 67 Min: 39.298 Mean: 74.981 Max: 112.808 StdDev: 15.765 Mode: 66.667 (21) Bins: 15 Bin Width: 13.333	 L = 142.559	 Count: 108 Min: 95.367 Mean: 142.559 Max: 203.467 StdDev: 22.783 Mode: 133.333 (44) Bins: 15 Bin Width: 26.667
		 W = 72.031	 Count: 73 Min: 46.075 Mean: 72.031 Max: 105.206 StdDev: 12.408 Mode: 66.667 (30) Bins: 15 Bin Width: 13.333	 L = 139.367	 Count: 150 Min: 84.264 Mean: 139.367 Max: 212.118 StdDev: 24.003 Mode: 133.333 (66) Bins: 15 Bin Width: 26.667
		 W = 75.394	 Count: 107 Min: 49.055 Mean: 75.394 Max: 111.417 StdDev: 12.277 Mode: 66.667 (49) Bins: 15 Bin Width: 13.333	 L = 145.252	 Count: 177 Min: 93.398 Mean: 145.252 Max: 194.115 StdDev: 21.786 Mode: 133.333 (78) Bins: 15 Bin Width: 26.667

5	158 x 158 x 76		 Count: 69 Min: 54.056 Mean: 79.438 Max: 110.056 StdDev: 13.037 Mode: 80 (27) Bins: 15 Bin Width: 13.333		 Count: 82 Min: 116.081 Mean: 163.415 Max: 214.855 StdDev: 20.367 Mode: 160 (40) Bins: 15 Bin Width: 26.667
		W = 79.438 	 Count: 76 Min: 48.103 Mean: 77.193 Max: 100.729 StdDev: 11.613 Mode: 66.667 (28) Bins: 15 Bin Width: 13.333	L = 163.415 	 Count: 88 Min: 85.306 Mean: 151.806 Max: 209.729 StdDev: 23.676 Mode: 133.333 (35) Bins: 15 Bin Width: 26.667
		W = 77.193 	 Count: 104 Min: 35.019 Mean: 70.091 Max: 103.826 StdDev: 14.631 Mode: 53.333 (33) Bins: 15 Bin Width: 13.333	L = 151.806 	 Count: 134 Min: 102.135 Mean: 157.500 Max: 222.844 StdDev: 23.294 Mode: 133.333 (55) Bins: 15 Bin Width: 26.667
		W = 70.091		L = 157.500	
6	163 x 163 x 80		 Count: 89 Min: 54.613 Mean: 81.522 Max: 110.741 StdDev: 13.074 Mode: 80 (30) Bins: 15 Bin Width: 13.333		 Count: 39 Min: 85.139 Mean: 155.637 Max: 227.991 StdDev: 31.319 Mode: 160 (13) Bins: 15 Bin Width: 26.667
		W = 81.522		L = 155.637	

		 W = 76.265  W = 82.333	 Count: 31 Mean: 76.265 StdDev: 13.955 Bins: 15 Min: 49.523 Max: 101.110 Mode: 66.667 (11) Bin Width: 13.333  Count: 88 Mean: 82.333 StdDev: 11.929 Bins: 15 Min: 59.267 Max: 110.193 Mode: 80 (32) Bin Width: 13.333	 L = 164.960  L = 167.601	 Count: 120 Mean: 164.960 StdDev: 23.596 Bins: 15 Min: 103.607 Max: 237.577 Mode: 160 (46) Bin Width: 26.667  Count: 164 Mean: 167.601 StdDev: 28.315 Bins: 15 Min: 101.835 Max: 235.072 Mode: 160 (51) Bin Width: 26.667
1*	206x206x106 206±40 106±19	 W = 104.676  W = 109.623	 Count: 86 Mean: 104.676 StdDev: 17.374 Bins: 15 Min: 66.147 Max: 179.029 Mode: 93.333 (29) Bin Width: 13.333  Count: 117 Mean: 109.623 StdDev: 19.738 Bins: 15 Min: 76.057 Max: 174.367 Mode: 106.667 (33) Bin Width: 13.333	 L = 211.182  L = 204.016	 Count: 77 Mean: 211.182 StdDev: 44.224 Bins: 15 Min: 140.928 Max: 333.896 Mode: 186.667 (23) Bin Width: 26.667  Count: 73 Mean: 204.016 StdDev: 36.399 Bins: 15 Min: 132.353 Max: 277.031 Mode: 186.667 (18) Bin Width: 26.667

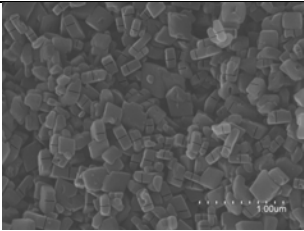
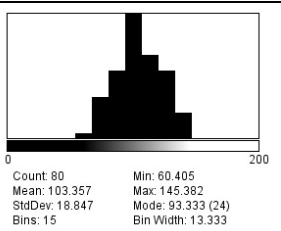
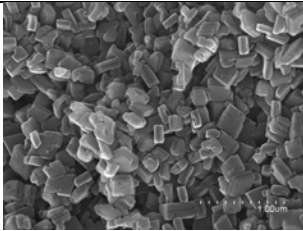
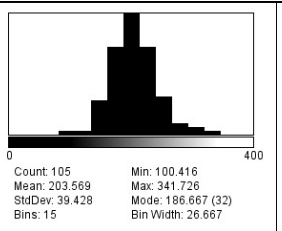
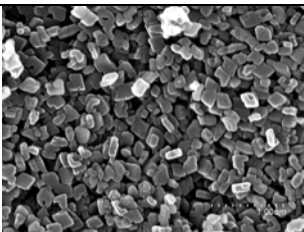
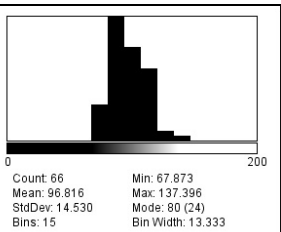
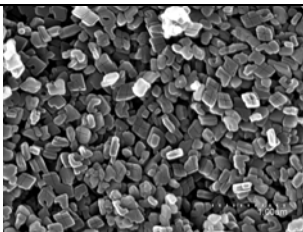
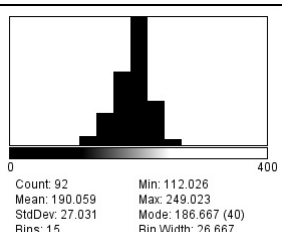
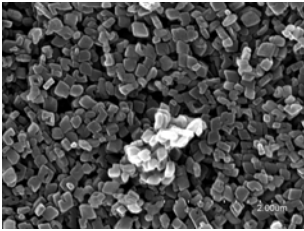
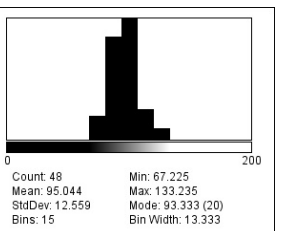
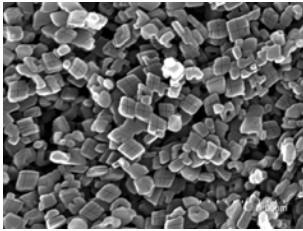
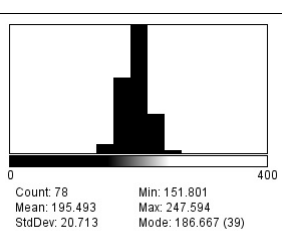
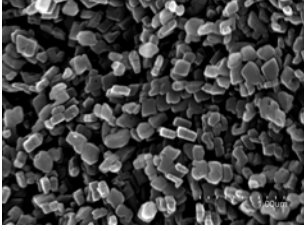
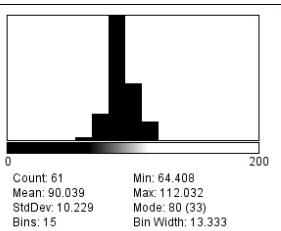
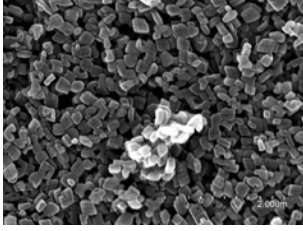
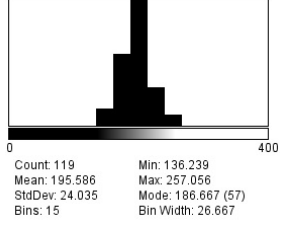
		 W = 103.357	 Count: 80 Mean: 103.357 StdDev: 18.847 Bins: 15 Min: 60.405 Max: 145.382 Mode: 93.333 (24) Bin Width: 13.333	 L = 203.569	 Count: 105 Mean: 203.569 StdDev: 39.428 Bins: 15 Min: 100.416 Max: 341.726 Mode: 186.667 (32) Bin Width: 26.667
2*	194 x 194 x 94 194±24 94±12	 W = 96.816	 Count: 66 Mean: 96.816 StdDev: 14.530 Bins: 15 Min: 67.873 Max: 137.396 Mode: 80 (24) Bin Width: 13.333	 L = 190.059	 Count: 92 Mean: 190.059 StdDev: 27.031 Bins: 15 Min: 112.026 Max: 249.023 Mode: 186.667 (40) Bin Width: 26.667
		 W = 95.044	 Count: 48 Mean: 95.044 StdDev: 12.559 Bins: 15 Min: 67.225 Max: 133.235 Mode: 93.333 (20) Bin Width: 13.333	 L = 195.493	 Count: 78 Mean: 195.493 StdDev: 20.713 Bins: 15 Min: 151.801 Max: 247.594 Mode: 186.667 (39) Bin Width: 26.667
		 W = 90.039	 Count: 61 Mean: 90.039 StdDev: 10.229 Bins: 15 Min: 64.408 Max: 112.032 Mode: 80 (33) Bin Width: 13.333	 L = 195.586	 Count: 119 Mean: 195.586 StdDev: 24.035 Bins: 15 Min: 136.239 Max: 257.056 Mode: 186.667 (57) Bin Width: 26.667

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

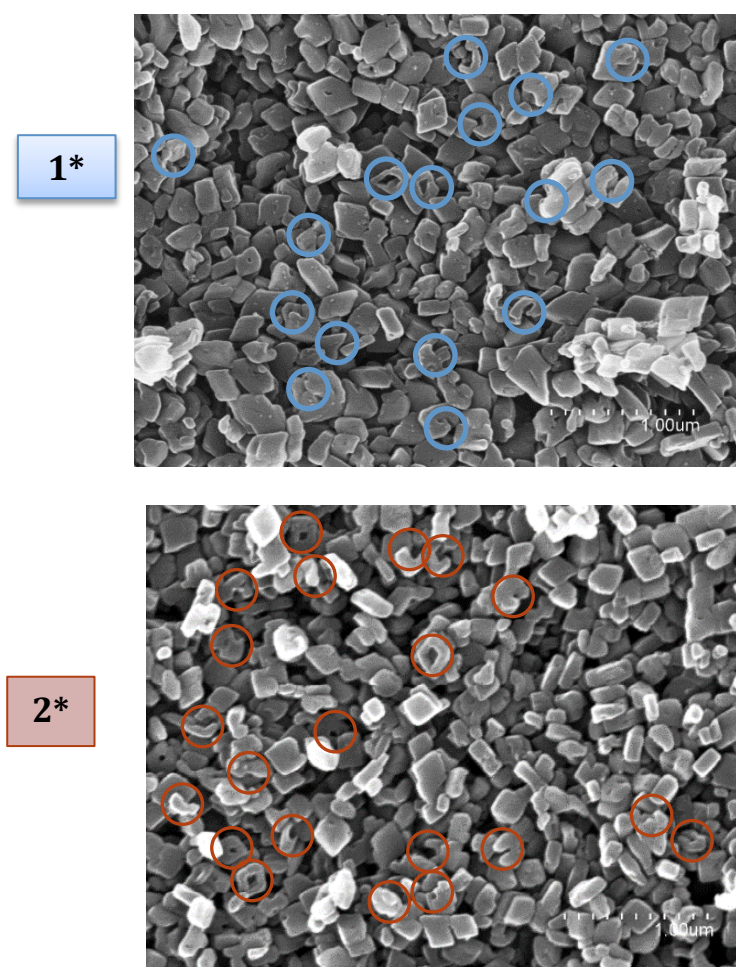


Figure S3. Powder x-ray diffraction patterns of $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ at 293 K: calculated from the crystal structure^[33d] and the nanocrystals **1-6** (experimental).

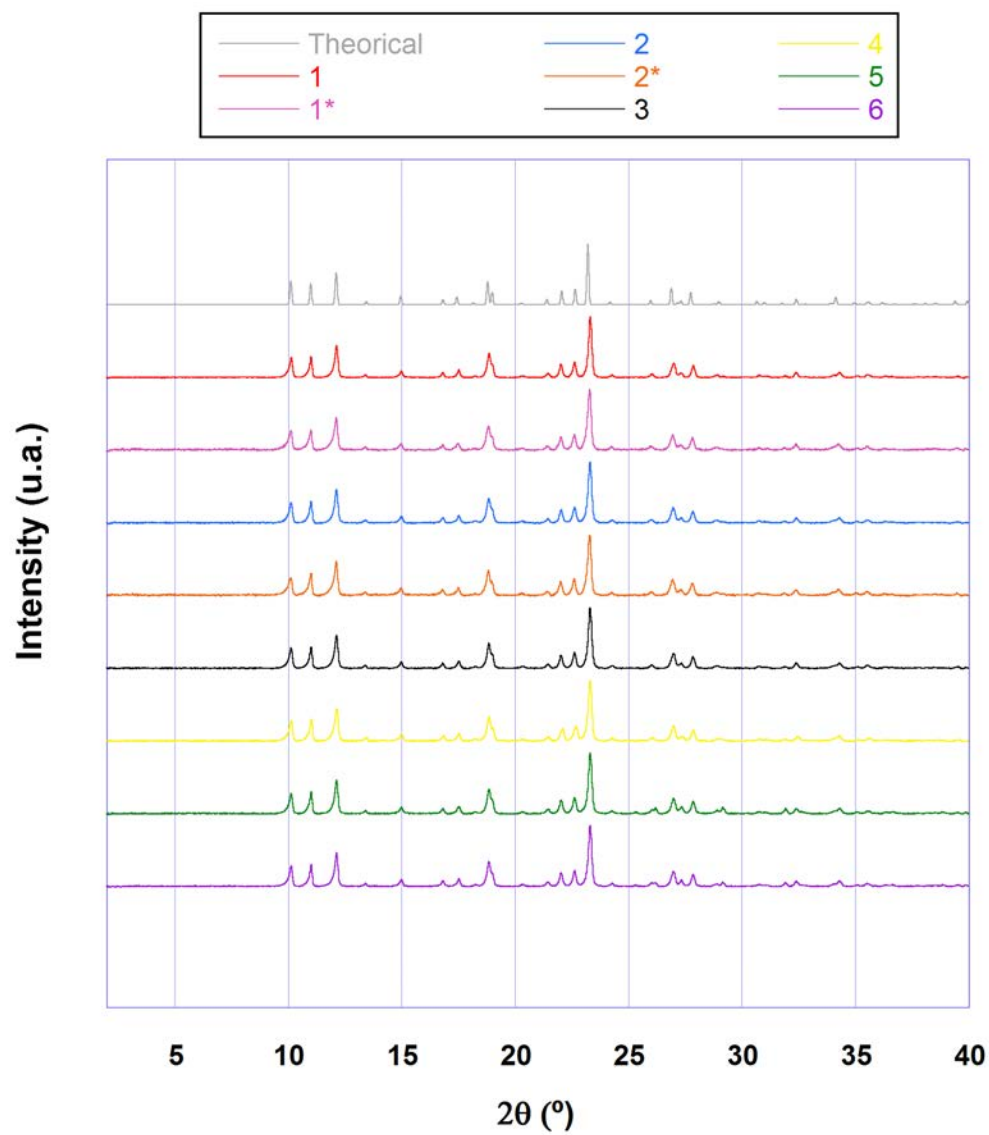
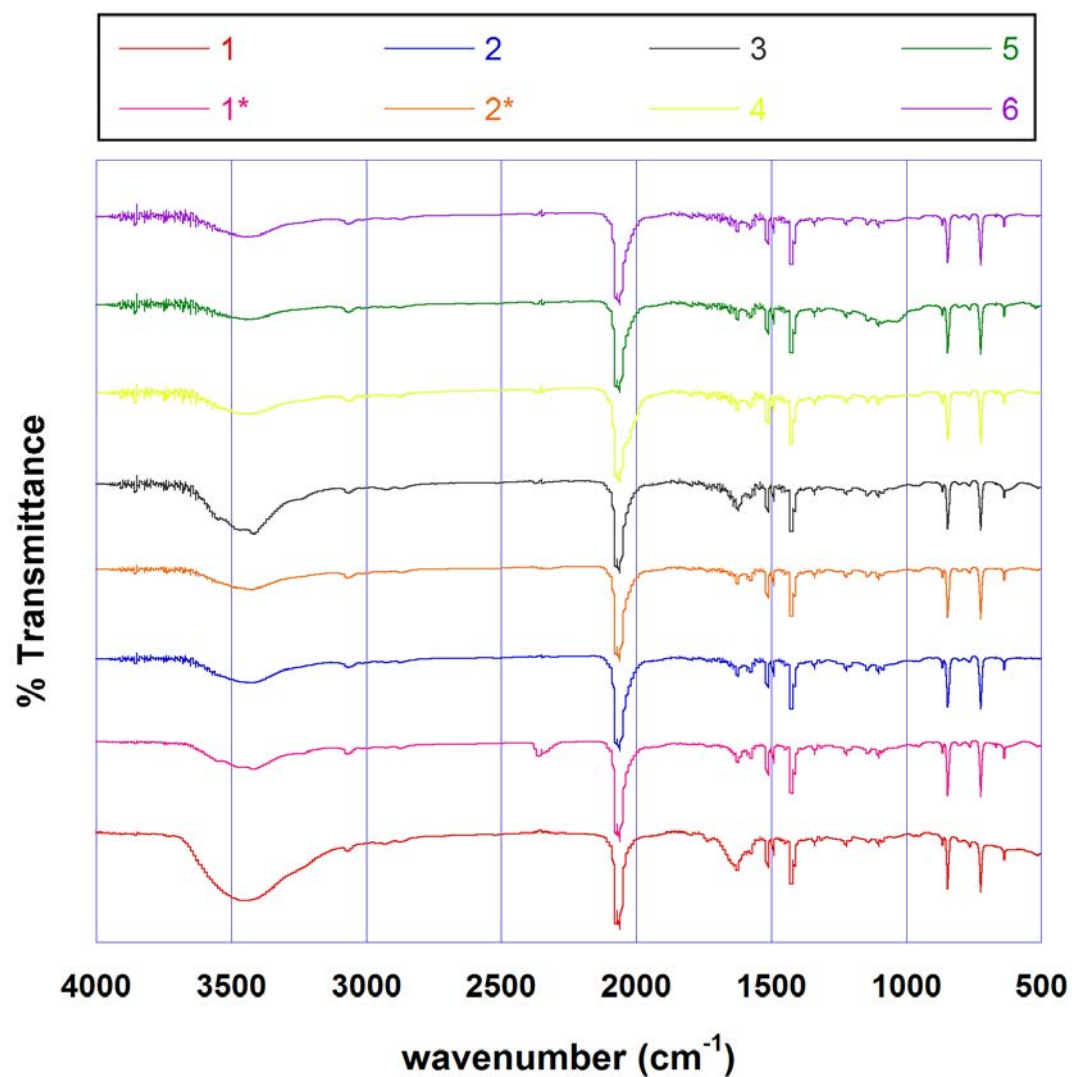


Figure S4. IR spectra recorded at 293 K for **1-6**, **1*** and **2*** (a) and for sodium bis-(2-ethylhexyl) sulfosuccinate (NaOT) (b).

(a)



(b)

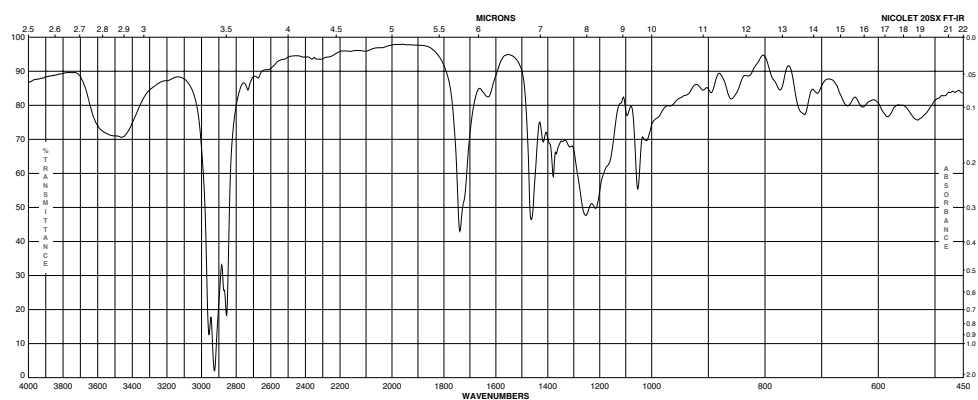


Figure S5. Mössbauer spectra of a reproduction of nanocrystals **1**, synthesis **1***, measured at 293 and 84 K (blue: LS doublet; red: HS doublet). (δ_{HS}): 0.985(5) mms^{-1} ; ($\Delta E_{\text{Q, HS}}$): 2.650(1) mms^{-1} . (δ_{LS}): 0.463(3) mms^{-1} ; ($\Delta E_{\text{Q, LS}}$): 0.360(5) mms^{-1} . 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: $\Gamma(\text{HS}) = 0.136(9) \text{ mm/s}$ and $\Gamma(\text{LS}) = 0.141(5) \text{ mm/s}$.

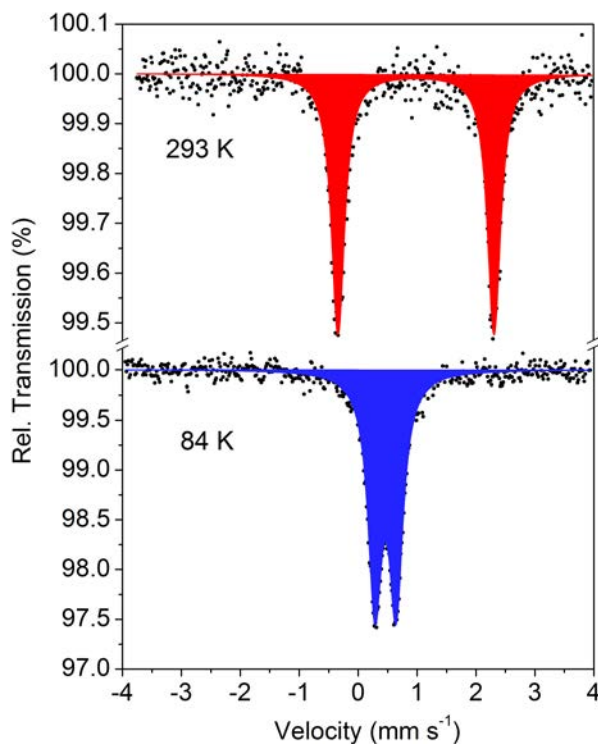


Table S3. Summary on crystallite sizes for 1-6 obtained from Scherrer's equation using the reflections (002), (110), (111) and (023). The parameter K was fixed at the value of 1, the $\lambda_\alpha = 1,540598$ Å and the standard used to calibrate the instrumental broadening was LaB₆.

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	(2 θ)	B obs. (2 θ)	B std. (2 θ)	B strc. (2 θ)	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	(2 θ)	B obs. (2 θ)	B std. (2 θ)	B strc. (2 θ)	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	(2 θ)	B obs. (2 θ)	B std. (2 θ)	B strc. (2 θ)	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	(2 θ)	B obs. (2 θ)	B std. (2 θ)	B strc. (2 θ)	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	(2 θ)	B obs. (2 θ)	B std. (2 θ)	B strc. (2 θ)	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	(2 θ)	B obs. (2 θ)	B std. (2 θ)	B strc. (2 θ)	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.

