

## Electronic Supplementary Information

### Water Stable Colloidal PVP coated Spin Crossover Nanoparticles

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## Experimental Section

### Materials

All manipulations were performed under aerobic conditions using reagents and solvents (Alfa Aesar, Sigma Aldrich, Serva) as received. The ligands 1H-1,2,4-triazole (Htrz), 4-amino-4H-1,2,4-triazole (NH<sub>2</sub>trz), were purchased from Alfa Aesar, while the iron(II)tetrafluoroborate hexahydrate salt, Fe(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O, the zinc(II)tetrafluoroborate hexahydrate salt, Fe(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O, and polyvinylpyrrolidone (PVP) from Sigma Aldrich.

### Synthesis of the NPs

#### **NPs 1. [Fe(Htrz)<sub>2</sub>(trz)](BF<sub>4</sub>)·1.4PVP**

A suspension of solid Fe(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.338 g, 1.00 mmol) and PVP (0.070 g) in 5 mL EtOH was added to a solution of solid Trz (0.207 g, 3 mmol) and PVP (0.070 g) in 5 mL EtOH. The obtained suspension was stirred for ~2 h resulting in violet color. The precipitated nanoparticles were isolated by centrifugation at 6000 rpm, washed several times with EtOH and dried in the air.

#### **NPs 2. [Fe<sub>0.8</sub>Zn<sub>0.2</sub>(Htrz)<sub>2</sub>(trz)](BF<sub>4</sub>)·1.3PVP**

A suspension of solid Fe(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.270 g, 0.80 mmol), Zn(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.069 g, 0.20 mmol) and PVP (0.070 g) in 5 mL EtOH was added to a solution of solid Trz (0.207 g, 3 mmol) and PVP (0.070 g) in 5 mL EtOH. The obtained suspension was stirred for ~2 h resulting in pale violet color. The precipitated nanoparticles were isolated by centrifugation at 6000 rpm, washed several times with EtOH and dried in the air.

#### **NPs 3. [Fe(Htrz)<sub>2</sub>(trz)<sub>0.7</sub>(NH<sub>2</sub>trz)<sub>0.3</sub>](BF<sub>4</sub>)<sub>1.3</sub>·0.6PVP**

A suspension of solid Fe(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.338 g, 1.00 mmol) and PVP (0.070 g) in 5 mL EtOH was added to a solution of solid Trz (0.186 g, 2.7 mmol), NH<sub>2</sub>trz (0.025 g, 0.3 mmol) and PVP (0.070 g) in 5 mL EtOH. The obtained suspension was stirred for ~2 h resulting in pale violet color. The precipitated nanoparticles were isolated by centrifugation at 6000 rpm, washed several times with EtOH and dried in the air.

## Physical Measurements

Elemental analyses (C, H, N) were performed by the in-house facilities of the University of Patras (Greece). IR spectra ( $4000\text{-}400\text{ cm}^{-1}$ ) were recorded using a Perkin-Elmer 16PC FT-IR spectrometer with samples prepared as KBr pellets. UV-Vis absorption spectra were recorded between 280 and 1100 nm by using the spectrometer PGS-2 produced by Carl Zeiss. P-XRD measurements were collected on freshly prepared samples of the complexes on a Siemens D500 diffractometer using Cu  $K\alpha$  radiation. The measurements performed with the following combination of slits:  $1.0^\circ/1.0^\circ/1.0^\circ$  as aperture diaphragms,  $0.15^\circ$  as detector diaphragm and  $0.15^\circ$  as diffracted beam monochromator diaphragm. The measured  $2\theta$  range scanned in steps of  $0.03/3\text{s}$ . The accelerating voltage and applied current were 40 kV and 35 mA, respectively. TEM study performed utilizing a FEI CM20 TEM operating at 200 kV. TEM specimens prepared by drop casting a 3  $\mu\text{L}$  droplet of nanoparticles suspension in acetone on a carbon coated Cu TEM grid. The size of the particles determined by “manual counting” using ImageJ software (<https://imagej.net>). The direct-current (DC) magnetic susceptibility measurements were measured on powder samples using a physical-properties measurement system (PPMS, Quantum Design) at 2 – 300 K with a rate of  $0.5\text{ K min}^{-1}$  under an applied dc magnetic field of 1000 Oe. The experimental data were corrected for the diamagnetism and signal of the sample holder and the Pascal constants were used for the diamagnetic corrections. Differential Scanning Calorimetry (DSC) measurements were carried out in a N(g) atmosphere using a DSC (Q100, TA Instruments, USA) instrument. Aluminium hermetic pans were used to encapsulate 5-7 mg of sample. The pans were purged with nitrogen at a rate of  $50\text{ mL min}^{-1}$  and liquid nitrogen was used for cooling. Initially, the samples were cooled down from 200 K to 450 K at the maximum permissible rate by the instrument. Then the samples were subjected to two successive thermal regimes; (a) heating from 200 K to 450 K at a rate of  $1\text{ K min}^{-1}$  and (b) cooling to 200 K at the same rate. At the beginning and end of each heating and cooling run the sample was held isothermally for 5 min. DLS measurements were performed using an Amerigo Particle Size & Zeta Potential Analyzer from Cordouan Technologies. The sample was measured by external in-situ probe in a 10 mL lab tube at ambient temperature. The intensity size distribution was obtained using the cumulant fit on 5 minutes long measurement. Data for long term measurements were obtained every 30 minutes for  $\sim 2$  days and the last control measurement was performed after 7 days.

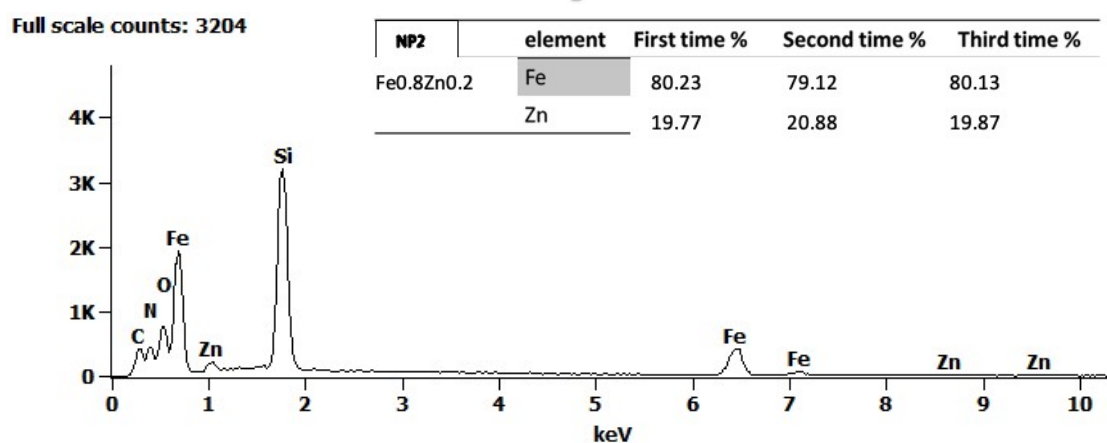
To sum up, physical and structural characterization of the NPs was carried out with Infrared (IR) Spectroscopy and X-ray Powder Diffraction (p-XRD), while Differential Scanning Calorimetry (DSC) studies were also applied for each case in order to determine the SCO behavior in solid state. Transmission Electron Microscopy (TEM)

was used in order to define the shape and size of the NPs, while UV-Vis Spectroscopy (UV-Vis) was used for gathering important data collection regarding the NPs behavior in their aqueous dispersions.

## Elemental Analyses

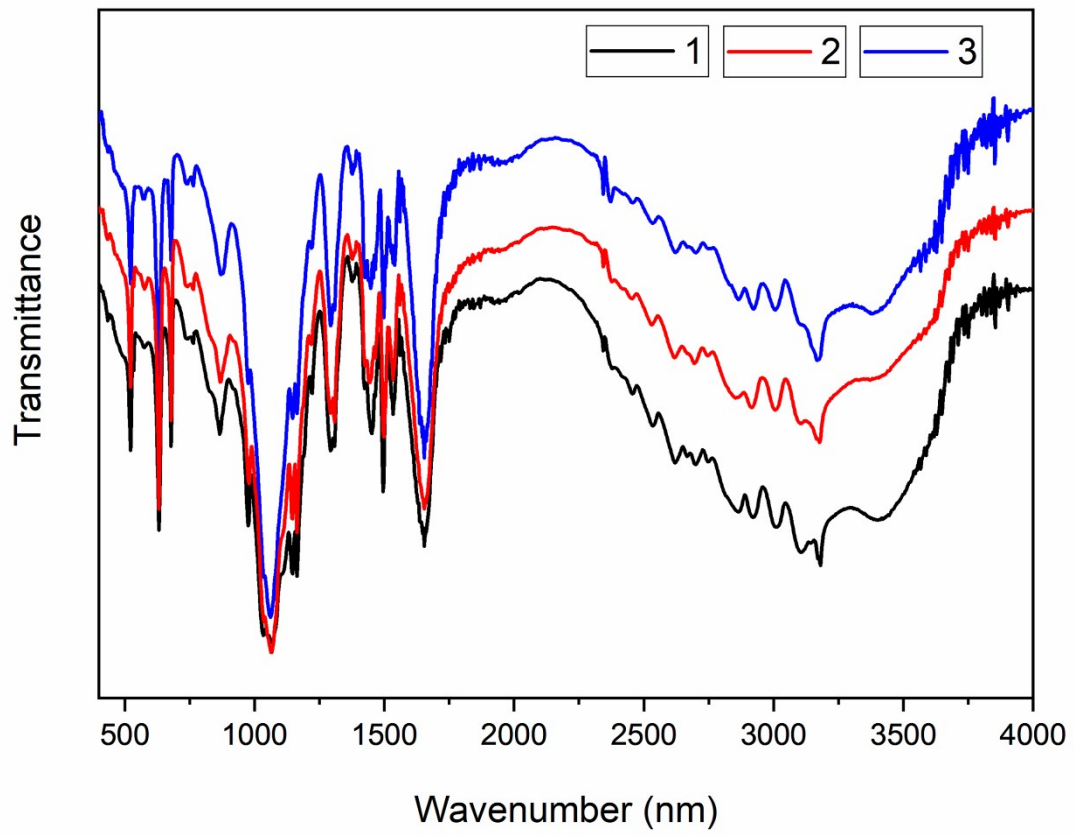
**Table S1.** Elemental analyses for compounds **1 - 3**.

Sample		C [%]	N [%]	H [%]	Molecular Formulae
<b>1</b>	exptl	<b>34.42</b>	<b>28.66</b>	<b>4.26</b>	$[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4) \cdot 1.4\text{PVP}$
	calcd	34.25	28.87	4.11	504 g/mol
<b>2</b>	exptl	<b>33.58</b>	<b>29.01</b>	<b>4.12</b>	$[\text{Fe}_{0.8}\text{Zn}_{0.2}(\text{Htrz})_2(\text{trz})](\text{BF}_4) \cdot 1.3\text{PVP}$
	calcd	33.45	29.14	4.01	494 g/mol
<b>3</b>	exptl	<b>25.94</b>	<b>30.88</b>	<b>3.18</b>	$[\text{Fe}(\text{Htrz})_2(\text{trz})_{0.7}(\text{NH}_2\text{trz})_{0.3}](\text{BF}_4)_{1.3} \cdot 0.6\text{PVP}$
	calcd	25.81	31.06	3.09	446 g/mol



**Figure S1.** Iron(II) and Zinc(II) ion content for the **NP2** determined by energy dispersive spectroscope (EDS) of field-emission scanning electron microscope (3<sup>rd</sup> time). In the inset there is a table depicting the ion contents for all the measurements.

IR spectra



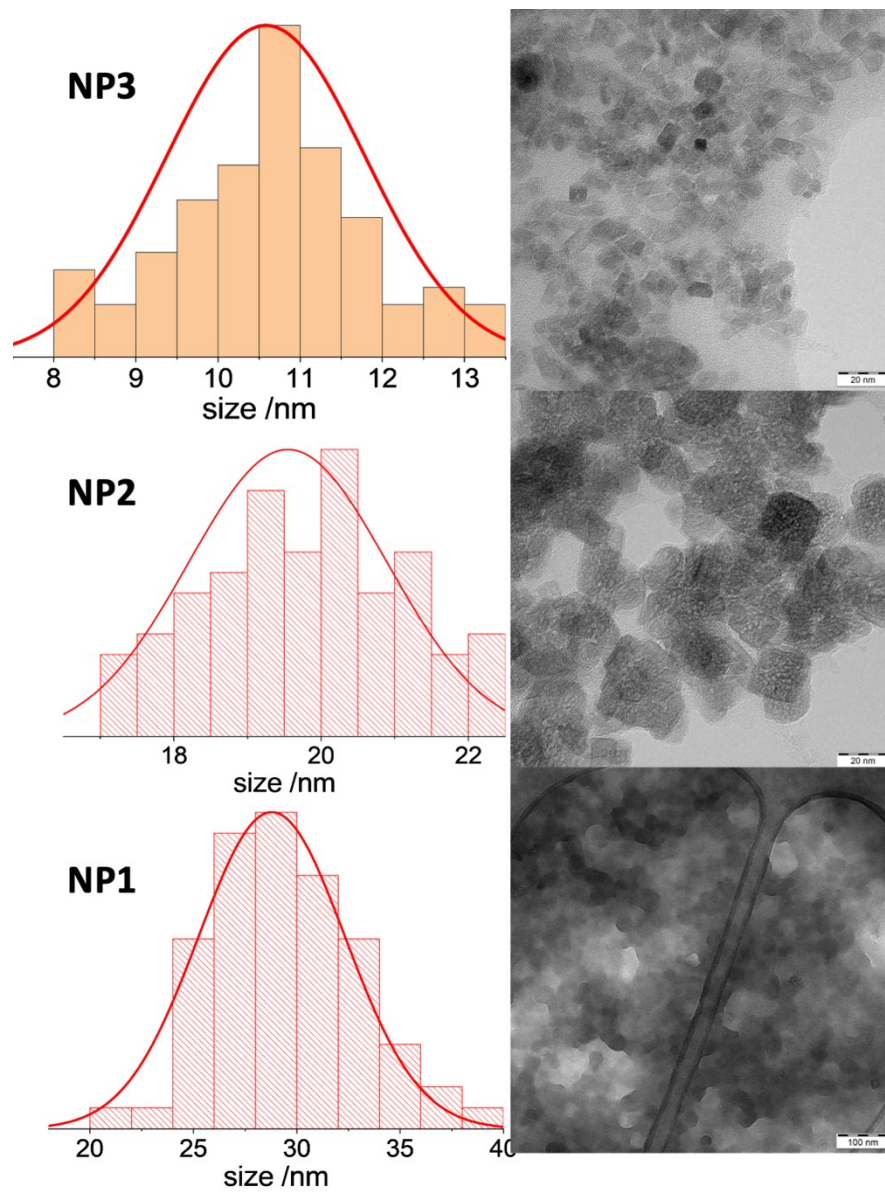
**Fig. S2.** IR spectra of the NP1 – 3 .

## Powder X-ray analysis

**Table S2.** Calculated nonstructural parameters based on Rietveld analysis using the Le Bail method for NP1 - 3.

NPs	a (Å)	b (Å)	c (Å)	V(Å <sup>3</sup> )
NP1	17.23(1)	7.20(1)	9.31(1)	1157.90
NP2	17.00(1)	7.45(1)	9.47(1)	1200.75
NP3	17.13(1)	7.37(1)	9.61(1)	1213.54

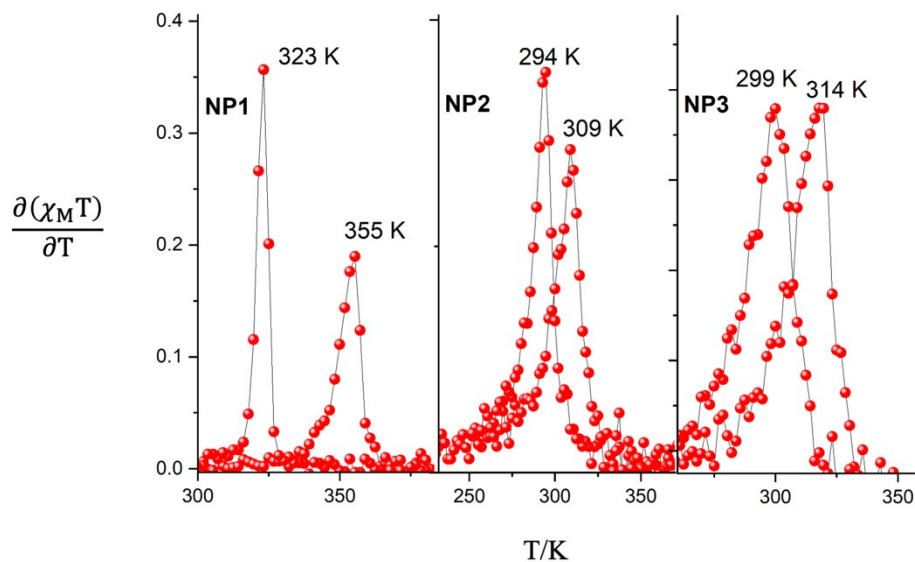
## TEM Microscopy



**Fig. S3.** Size distribution extracted from TEM images for NPs 1 - 3.



## Calculation of Critical Temperatures

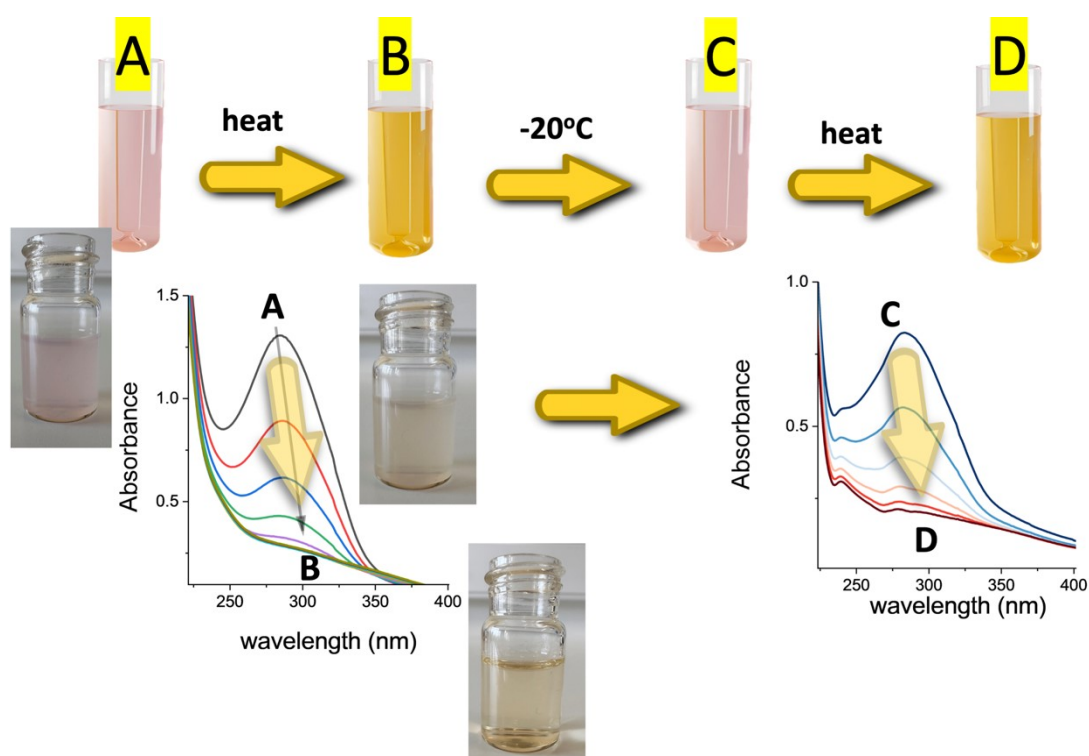


**Figure S4.** First derivatives of the magnetic susceptibility of **NP1-3** for the calculation of the critical temperatures.

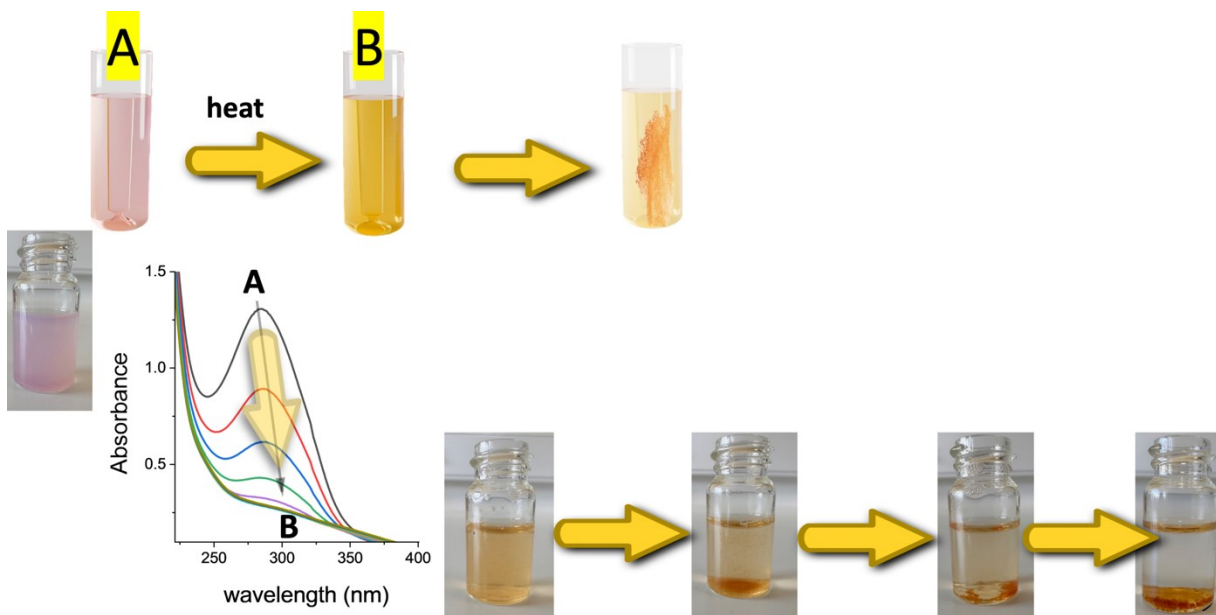
**Table S3.** Critical temperatures derived from the DSC measurements and from the thermal magnetic hysteresis for the studied SCO NPs based on the derivatives of the susceptibility data.

NPs	DSC			MAGNETIC		
	T <sub>up</sub> (K)	T <sub>down</sub> (K)	ΔT (K)	T <sub>up</sub> (K)	T <sub>down</sub> (K)	ΔT (K)
NP1	357	318	39	355	323	32
NP2	308	295	13	309	294	15
NP3	310	297	13	314	299	15

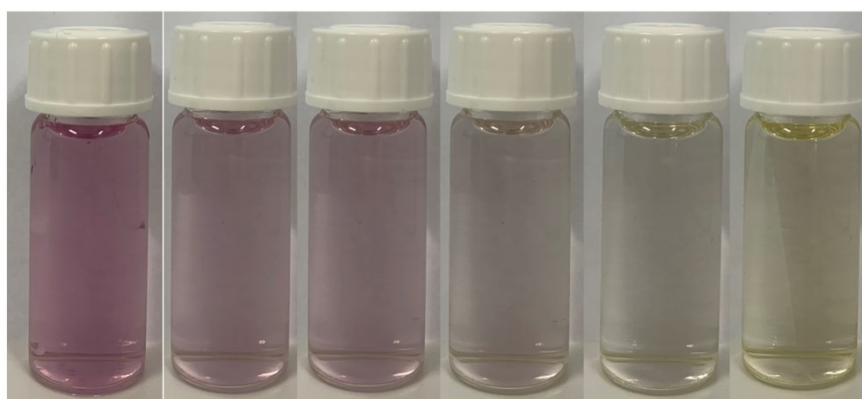
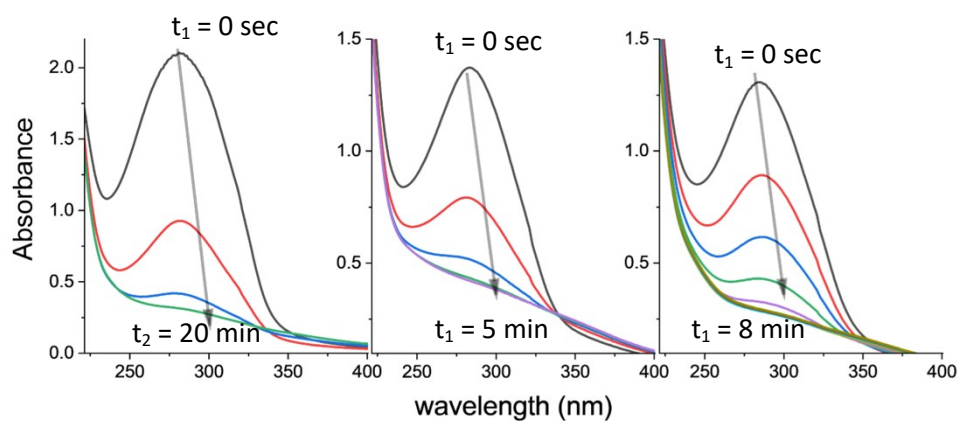
## UV-Vis Spectroscopy



**Fig. S4.** Application of **Protocol 1** for SCO NPs with the PVP as the stabilizing agent. The SCO NPs were dispersed in water (**A**), and the solution was heated to 70° C (**B**). The temperature dependence of the MLCT band at 280 nm is monitored, accompanied by a color change from violet (**A**) to yellow (**B**). The water dispersion (**B**) is cooled down to -20 °C, and the thawing procedure from -20 °C (**C**) to 70 °C (**D**) is monitored in the UV-Vis measurement of the MLCT band at 280 nm accompanied by color change from violet (**C**) to yellow (**D**). The protocol is repeated several times during six months without any change concerning the intensity of the MLCT band.

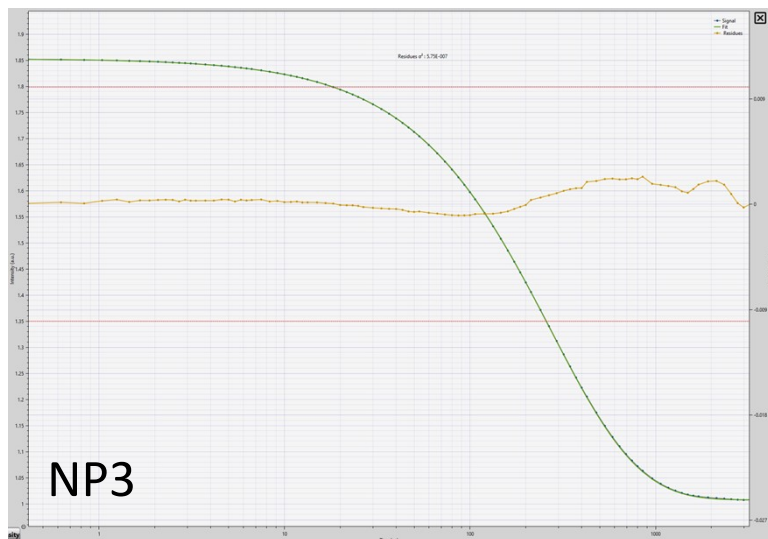
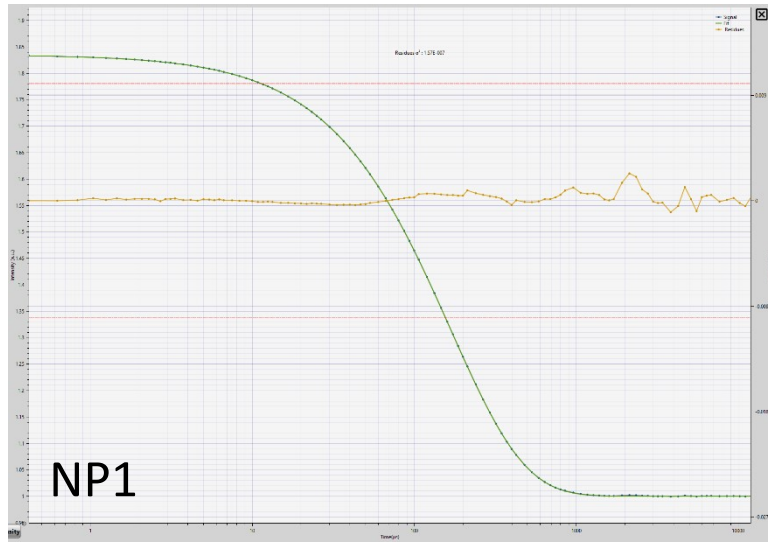


**Fig. S5.** Application of **Protocol 1** for SCO NPs without the PVP as the stabilizing agent. In this case, after the first heating to 70° C (**B**), sedimentation of colloidal SCO NPs occurred, which is accompanied by discoloration of the solution, verifying the oxidation of the Fe(II) ions.

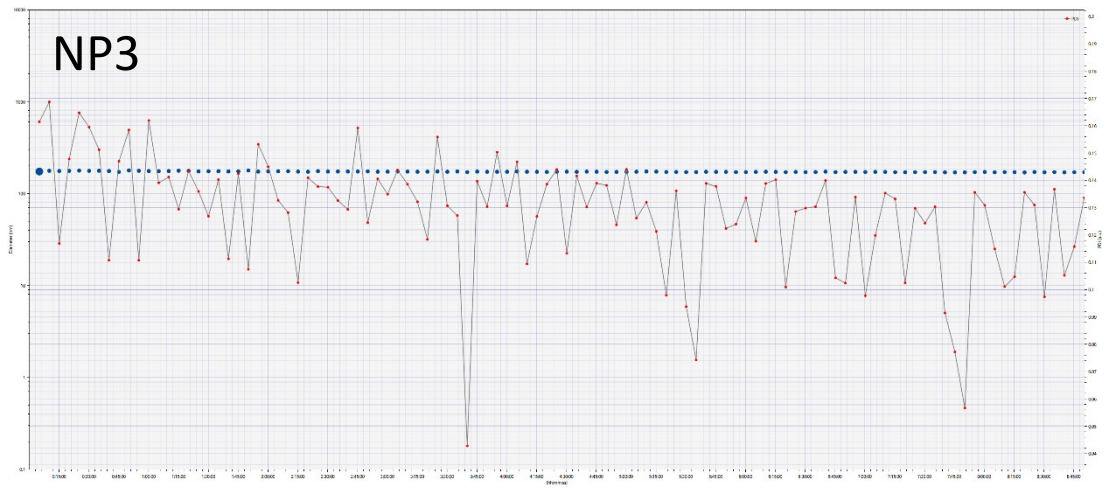
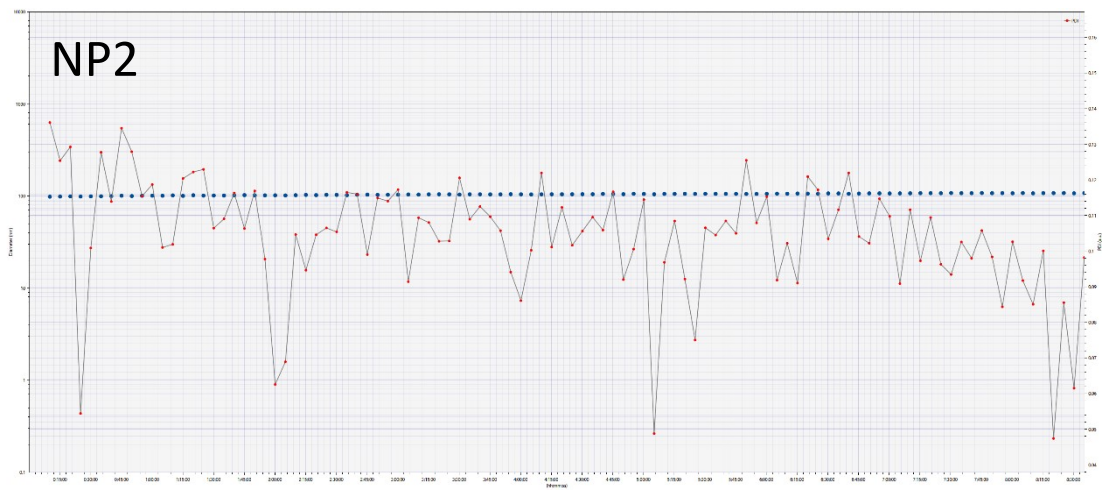
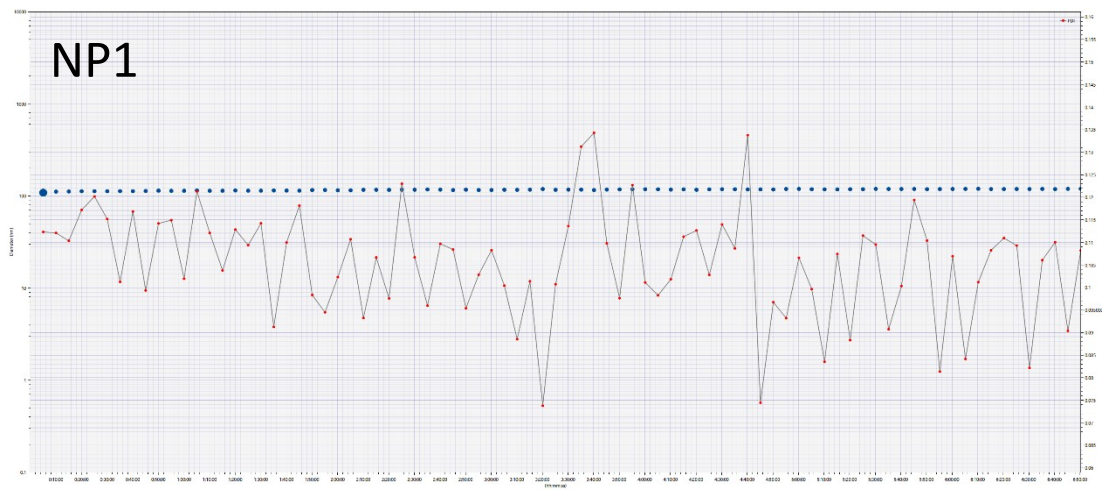


**Fig. S6. (upper)** UV-Vis spectra for NP1 – 3 immediately after sample dispersion in H<sub>2</sub>O (2 mg/3ml). The time duration of the evolution from the LS to HS state is 20, 5, and 8 min respectively. The absorption band around 280 nm corresponds to an MLCT transition when the Fe(II) is in the LS state while the disappearance of this transition is a direct evidence of a spin transition to a HS state (the time evolution of the UV experiment is following the direction of the arrow starting from t=0 sec to 20, 5, and 8 min respectively). **(lower)** the evolution of the color in the water dispersion of **NP1 – 3** immediately after sample dispersion in H<sub>2</sub>O. The water dispersion of the PVP protected 1D SCO coordination polymer [Fe<sup>II</sup>(Htrz)<sub>2</sub>(trz)](BF<sub>4</sub>) nanoparticles, **NP1-3**, is accompanied by a color change from violet to yellow denoting a change of the spin state from LS to a HS.

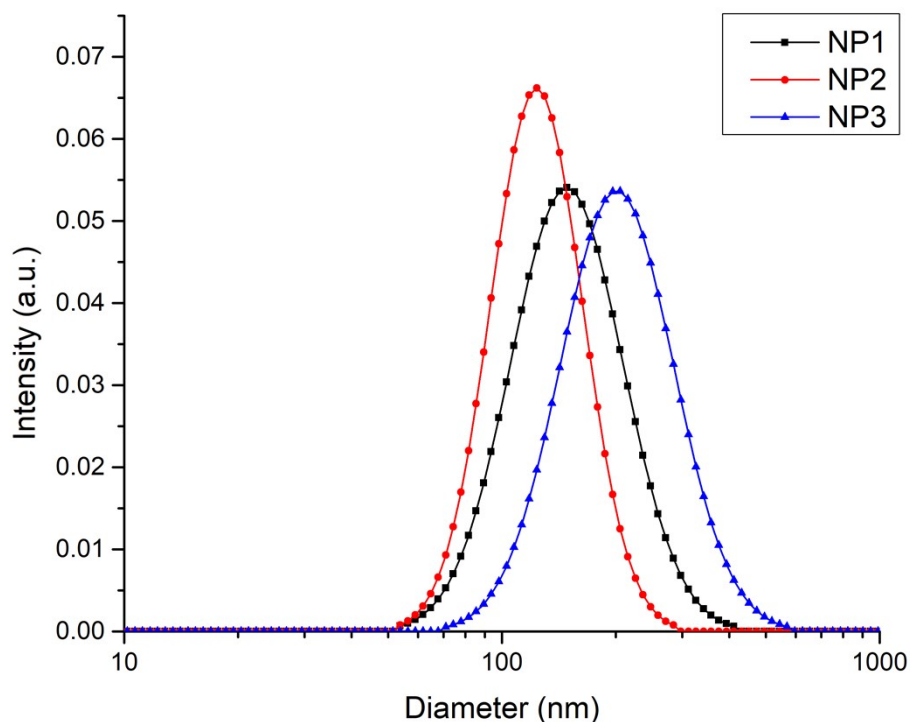
# DLS measurements



**Fig. S7** Autocorrelation function and residues for initial size distribution measurements in Fig. 2. The green line is the fit and residues are in yellow.



**Fig. S8** Time evolution of size distributions. Blue dots represent Z-average and red dots are the respective PDI. In two days NP1 maintained Z-average size between 108-120 nm and PDI under 0.12 ; NP2 maintained Z-average size between 98-107 nm and PDI under 0.14 ; NP3 maintained Z-average size between 170-178 nm and PDI under 0.17.



**Fig. S9** Size distributions after 7 days for: NP1 with Z-average = 125 nm, mean size = 157 nm and PDI = 0.12 ; NP2 with Z-average = 110 nm, mean size = 128 nm and PDI = 0.08 ; NP3 with Z-average = 169 nm, mean size = 213 nm and PDI = 0.13.