

Supplementary Information

A Step-Heating Procedure for the Synthesis of High-Quality FePt Nanostars

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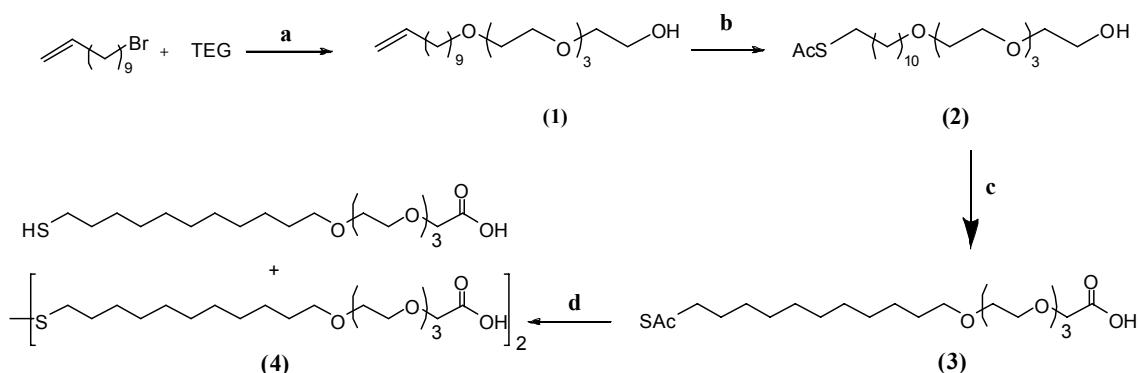
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S1. Chemicals and Characterization.

Platinum acetylacetone ($\text{Pt}(\text{acac})_2$) (/99%), Iron acetylacetone ($\text{Fe}(\text{acac})_2$) (99,95%), Oleic acid (90%), oleylamine (>70%), benzyl ether (99%), tetraethylene glycol (99%), sodium hydroxide and 11-bromoundec-1-ene (99%), Chromium (VI) oxide (CrO_3), Sulfuric acid (H_2SO_4 96%), Sodium methoxide (NaOMe) were purchased from Aldrich. All the reagents were used as received.

The size and morphologies of the resulting nanocrystals were determined by a JEOL-2100F transmission electronic microscope (TEM) operating at 200kV. All the measurements were performed on the original aliquots without any size sorting. The magnetic hysteresis measurements have been carried out by using superconducting quantum interference device (SQUID) magnetometer with magnetic field up to 9 T. The composition analysis was done by energy dispersive X-ray detector (EDX). UV-Vis spectra were recorded in a Beckman-Coulter DU 800 spectrophotometer and FT-IR spectra were acquired in a Thermo Nicolet FT-IR spectrometer.

S2. Synthesis of linker SH-C₁₁-TEG-CO₂H (4).



Scheme S2. Reagents and conditions. a) NaOH (50%), 100°C, 16h. b) AcSH, AIBN, THFdry, reflux, 3h . C) (1) Jones reagent, acetone, 30 min. D) (i) MeONa, MeOH, 15h (ii) amberlite IR-120.

Undecen-1-en-11-yltetra(ethylen glycol) (1).

A mixture of tetraethylenglycol (TEG) (35.6 g, 183.54 mmol, 4.2 eq) and NaOH (50%) (2.7 ml, 43.7 mmol, 1 eq) were stirred for $\frac{1}{2}$ h at 100°C. The reaction was cooled at room temperature and 11-Br-undecene (10.2 g, 43.7 mmol, 1 eq) was added. The reaction was heated at 100°C and left over night under stirring. The mixture was diluted with CH₂Cl₂ (20 ml), washed with water (40 ml) and extracted with hexane (3 x 40 ml). The hexane fractions were collected, dried over Na₂SO₄, filtered and the solvent evaporated at reduced pressure. The crude product (16 g) was purified by flash column chromatography on silica gel (eluent: EtOAc) to give **1** (10.46 g, 69%) as yellow oil.

R_f = 0.31 (EtOAc). ¹H RMN (CDCl₃, 500 MHz) 1.26-1.36 (m, 14H, 7xCH₂); 1.57-1.653 (m, 2H, CH₂); 2.01 (m, 2H). 2.7 (broad s, 1H, OH), 3.43 (t, 2H, J= 6.8 Hz, CH₂O); 3.72-3.55 (m, 16H, 4xOCH₂CH₂O), 4.97 (dd, 1H, J= 17.14, 2.06, -CH=CH₂), 4.90 (dd, 1H, J= 10.18, 9.09, -CH=CH₂), 5.78 (m, 1H, -CH=CH₂).

1-(Thioacetylundec-11-yl)tetra(ethylen glycol) (2).

To a solution of **5** (9.6 g, 27.7 mmol, 1 eq) in THF dry, AcSH (10.49 g, 138 mmol, 8 eq) and AIBN (cat.) were added. The mixture was left under reflux for 3 h. The reaction was diluted with 30 ml of EtOAc and a saturated solution of NaHCO₃ was added until neutral pH. The organic phase was washed with brine, dried over Na₂SO₄ and the solvent removed at reduced pressure. The residue was purified by flash column chromatography on silica gel (eluent: EtOAc/hexane 9:1 to EtOAc) to obtain **2** as colourless oil (7.8 g, 67%). **Rf** = 0.28 (EtOAc). **¹H RMN** (CDCl₃, 500 MHz) 1.247-1.364 (m, 14H, 7xCH₂); 1.527-1.672 (m, 4H, 2xCH₂); 2.656 (t, 2H, CH₂SS); 3.425 (t, 2H, CH₂O); 3.552-3.711 (m, 16H, 4xOCH₂CH₂O).

22-(Thioacetyl)-2,5,8,11-tetraoxadocosan-1-oic acid (3).

1 g of [1-(Methylcarbonyl)thio]undec-11-yl]tetra(ethylene glycol) **6** was dissolved in 5 mL acetone and Jones reagent was added drop by drop until green colour persisted. Then, the reaction was allowed to follow for 30 min and then it was stopped with 2-propanol, diluted with ethyl acetate, washed twice with water, and dried in the rotary evaporator. The purification was performed by column chromatography (CH₂Cl₂: MeOH 19:1) and 69% yield. **¹H NMR** (500 MHz, CDCl₃), δ 1.2-1.4 (m, 14H), 1.55 (qui, 4H, *J* = 7 Hz), 2.3 (s, 3H), 2.84 (t, 2H, *J* = 7 Hz), 3.4 (t, 2H, *J* = 7 Hz), 3.5-3.8 (m, 12H), 4.0 (s, 2H).

22-Mercapto [2,5,8,11- tetraoxadocosan]-1-oic acid and 23,23'-Dithio bis [2,5,8,11- tetraoxadocosan]-1-oic acid (4).

0.712 g of the protected product **7** were dissolved in 34 mL methanol and 0.088 g of sodium methoxide were added. The solution was stirred for 6 hours and then the pH

was neutralized with Amberlite IR120 H⁺. The reaction was filtrated, dried in the rotary evaporator and washed several times with diethyl ether. The final product **1** was obtained as a mixture of thiol and disulfide (39:61). 82% yield. **¹H NMR** (500 MHz, CDCl₃), δ 1.3-1.7 (m, 18H), 2.5 (t, 2H thiol, *J* = 7 Hz), 2.7 (t, 2H disulfide, *J* = 7 Hz) 3.5 (t, 2H, *J* = 14 Hz), 3.6-3.8 (m, 12H), 4.15 (s, 2H disulfide), 4.19 (s, 2H thiol).: **HR-MS** (pos., ionization phase MeOH) m/z: 416.2213 [M + 2Na]⁺² (C₃₈H₇₂O₁₂S₂Na₂ requires 416.2209).

S3. Ligand exchange reaction. In a general procedure, 2 mL of the solution of FePt nanostars (~0.033 mmol) were washed three times with ethanol, once with acetone, and were re-suspended in 8 mL of hexane. 500 μL of this solution (~2·10⁻³ mmol) were placed in a falcon tube and diluted to 2 mL. To this falcon tube were also added 2 mL of water containing 0.055 mmol of the amphiphilic linker SH-C₁₁-TEG-CO₂H (**3**) and 0.5 mmol of NaBH₄ to reduce disulfide groups in the linker. The tube was shaken overnight until the colours of the two phases changed indicating that the transfer was completed.

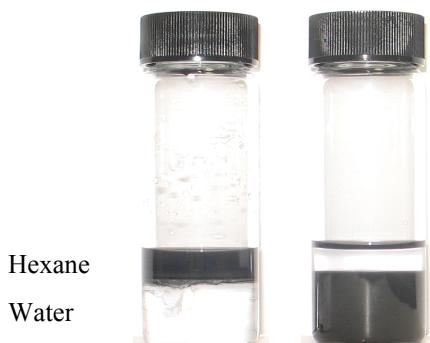


Figure S3. Ligand exchange reaction. Right, solutions before exchange (the coloured solution is the hexane phase); and left, solutions after shaking overnight.

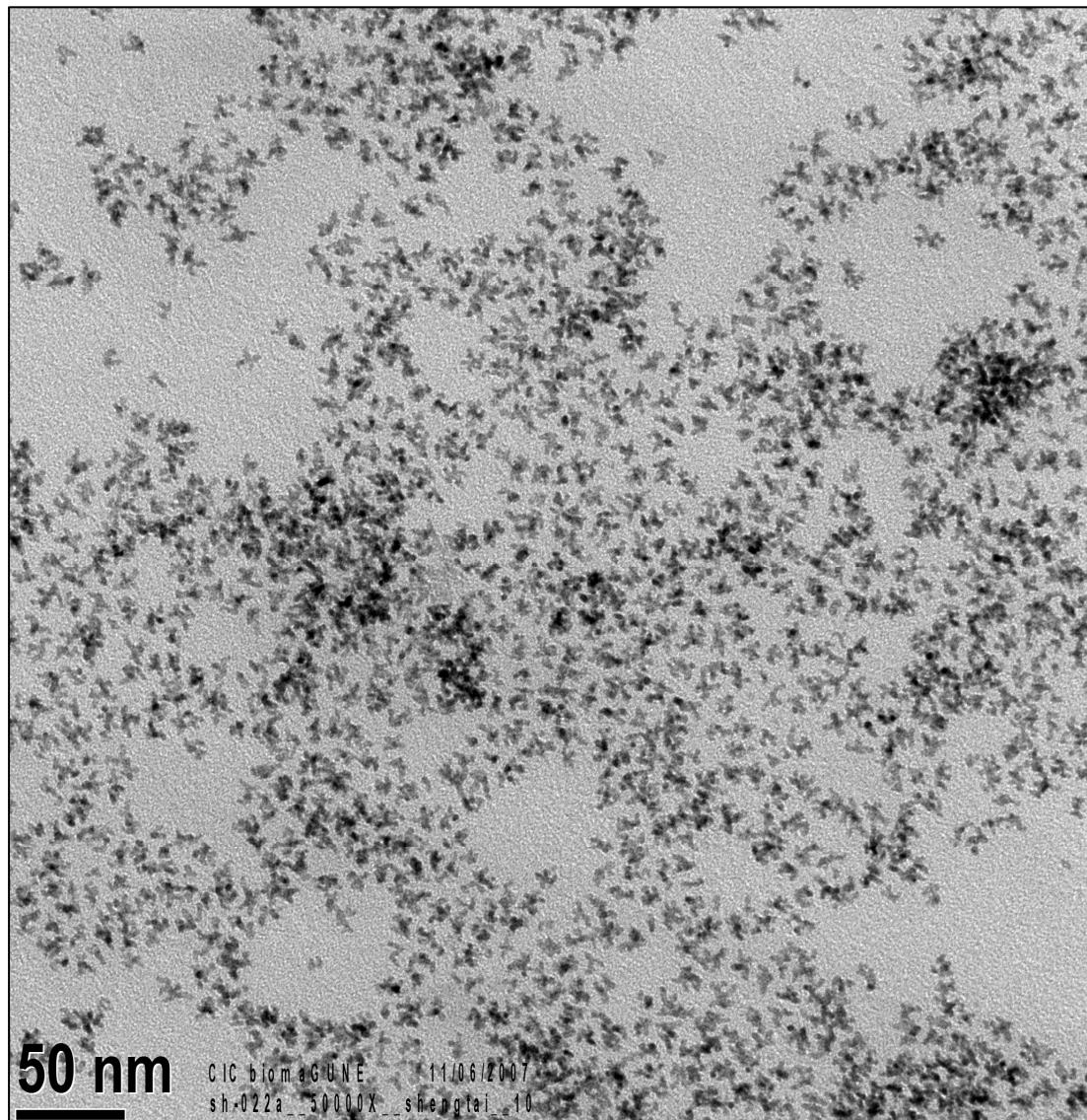


Figure S4. TEM overview of hexane soluble FePt nanostars synthesized.

S5. Synthesis of anisotropic shape FePt nanoparticles.

0.25 mmol Pt(acac)₂ were mixed with 20ml benzyl ether in a 50ml flask at room temperature under stirring. Once completely dissolved, 0.25 mmol Fe(acac)₂ were added, temperature is raised to 100°C to remove water under vacuum for 30min. The solution was bubbled with Ar for 30 min and heated at 120°C for 10 min, and 5 mmol (about 1.6ml) oleic acid is injected and 5 min later, 5mmol (about 2.35ml) oleylamine was also injected. The mixture solution was heated to 270°C at 10°C/min and kept at this temperature for 1 hour, and then was cooled down to room temperature by removing from heat source. PtFe nanorods were precipitated and washed twice with ethanol. The precipitates were re-dispersed in 10ml of hexane with 0.01 ml of oleic acid and oleylamine, respectively.

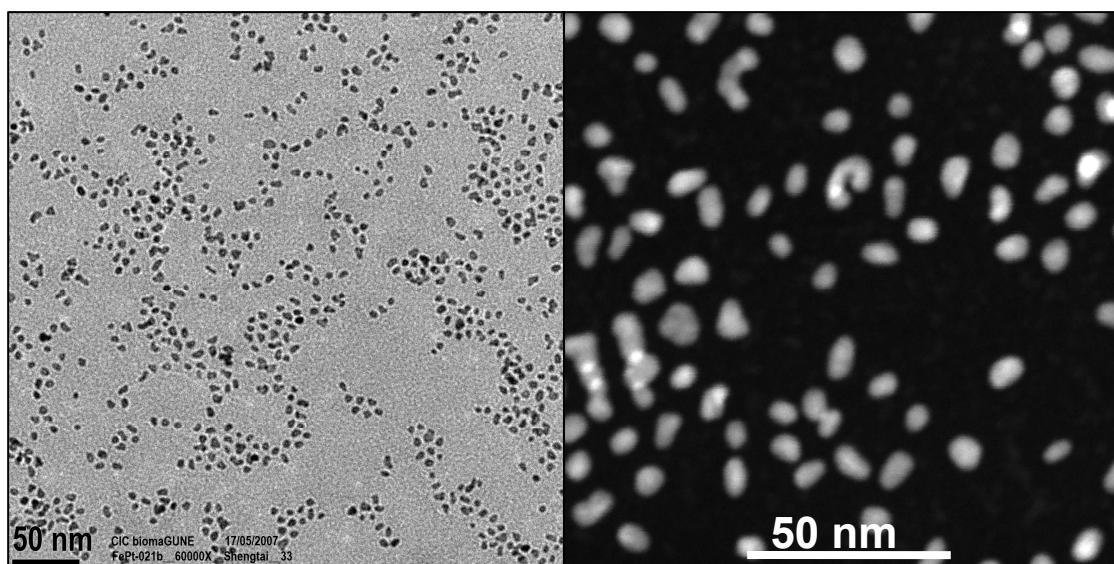


Figure S5. TEM (right) and STEM (left) image of anisotropic shaped FePt nanoparticles prepared by direct heating to 270°C.

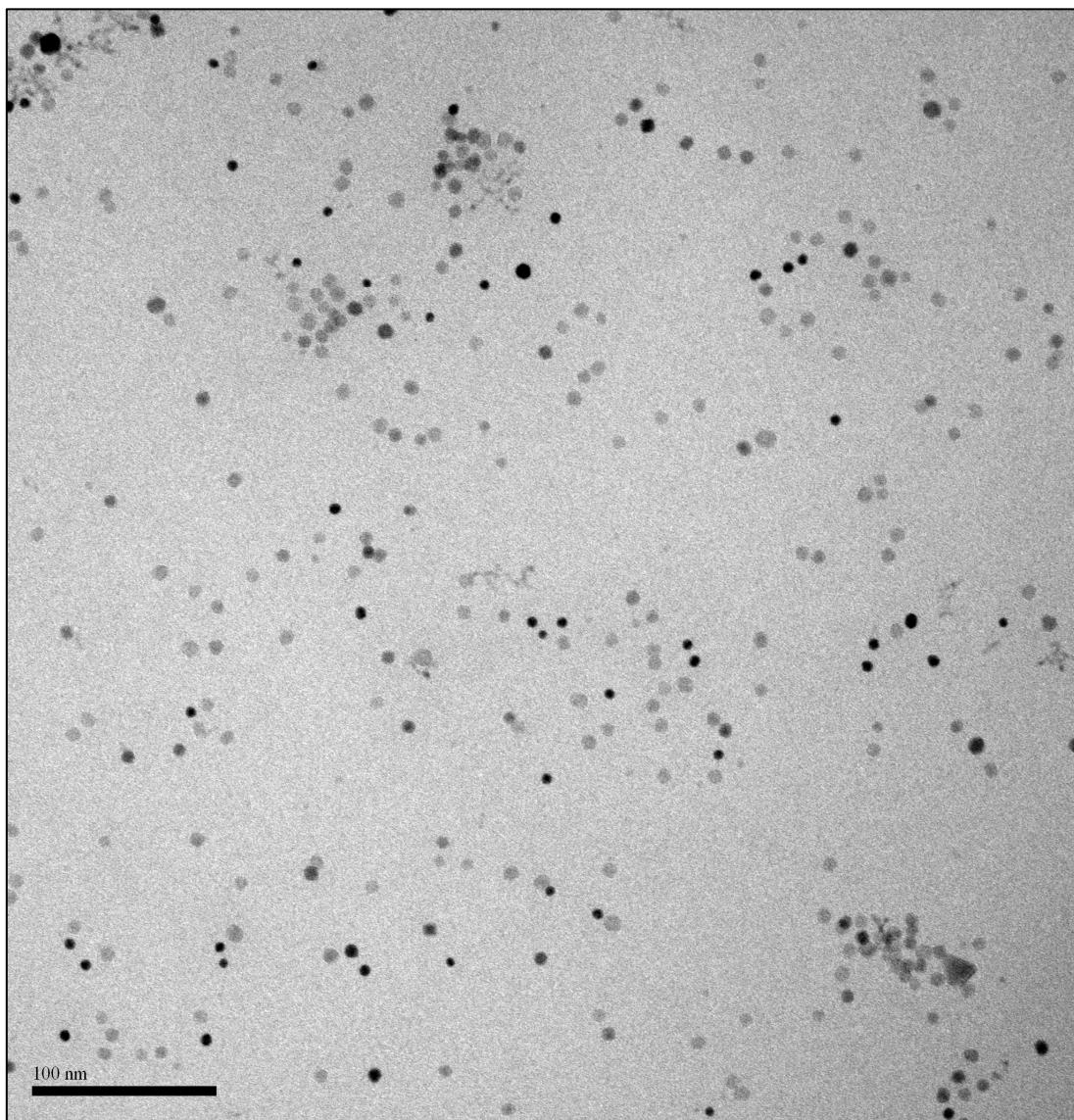


Figure S6. TEM micrograph of Pt nanoparticles obtained in the control experiment under the same conditions as for the FePt nanoparticles but in the absence of Fe (II) reagent.

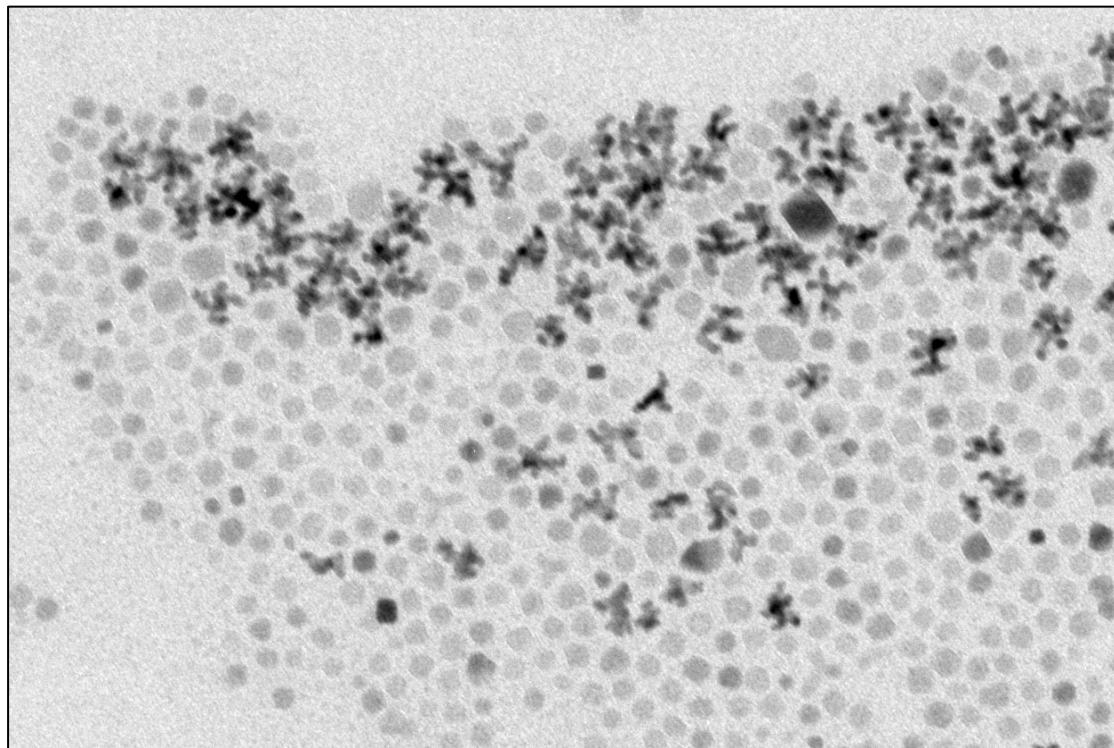


Figure S7. TEM micrograph of an aliquot of the preparation of FePt nanoparticles in hexane after 1 min at 240°C and before slow heating (10°C/10 min or 15°C/5 min) showing heterogeneous populations of nanoparticles.

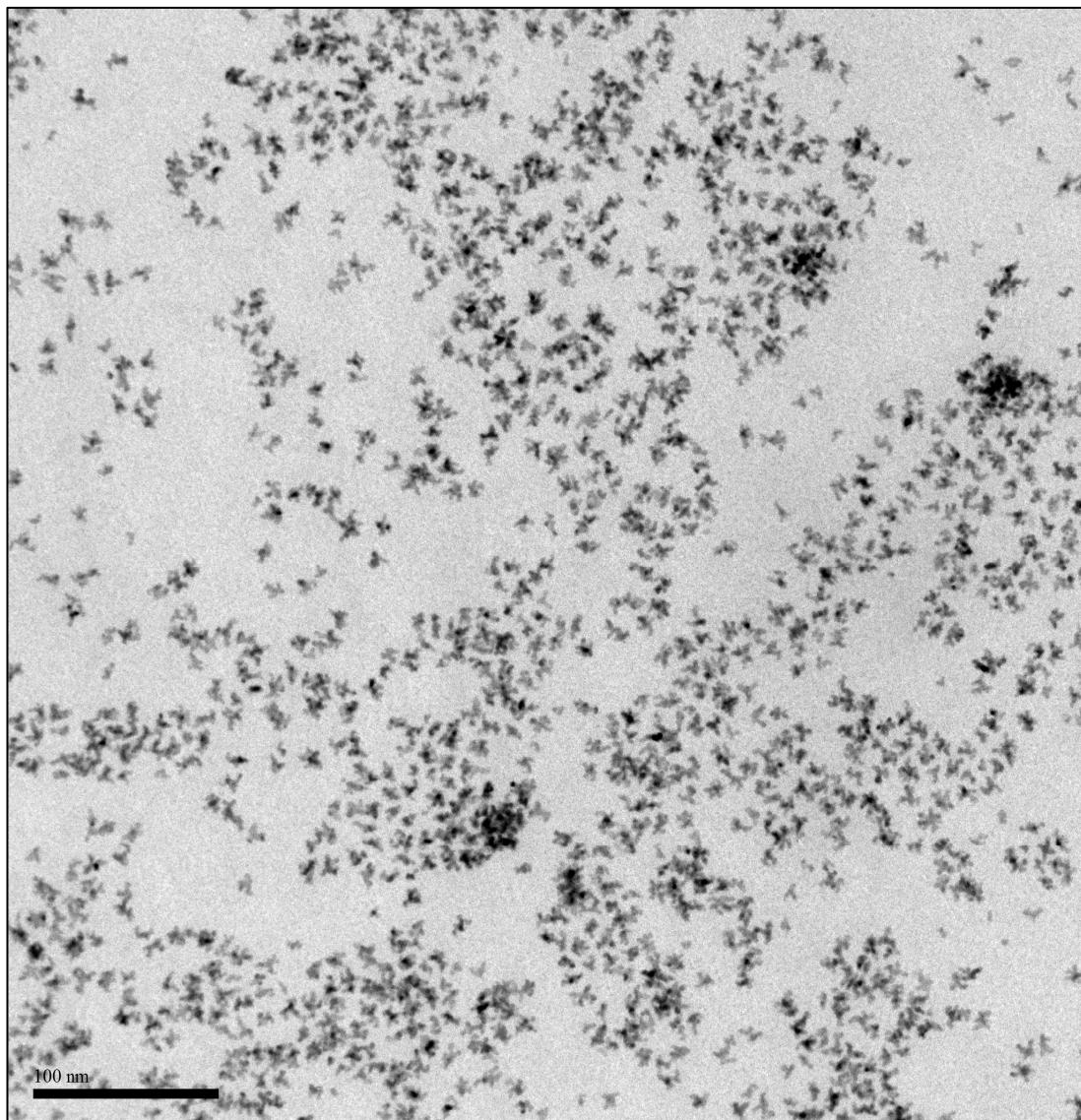


Figure S8 a. TEM micrograph of water soluble FePt nanostars.

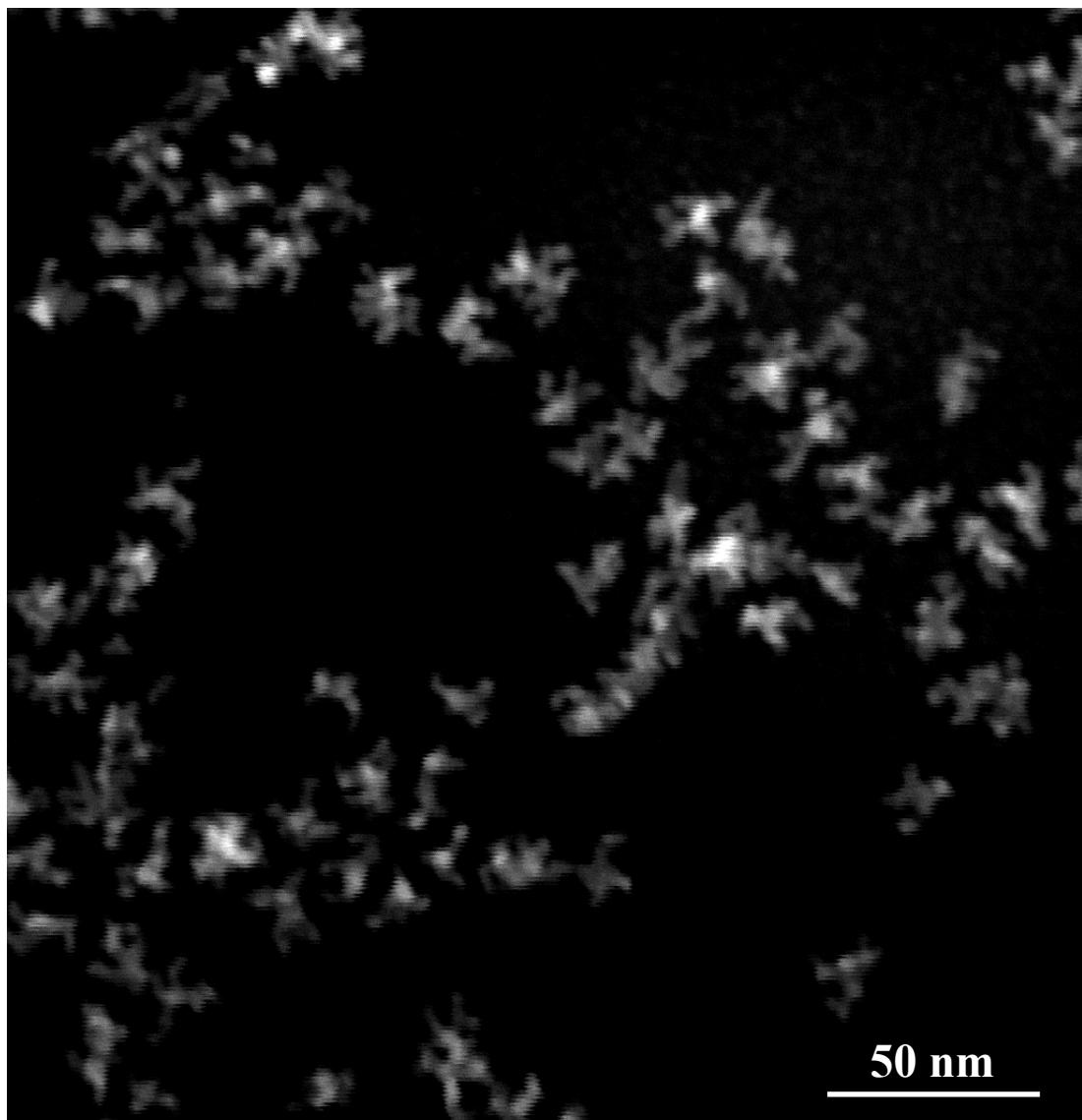


Figure S8 b. STEM micrograph of water soluble FePt nanostars.

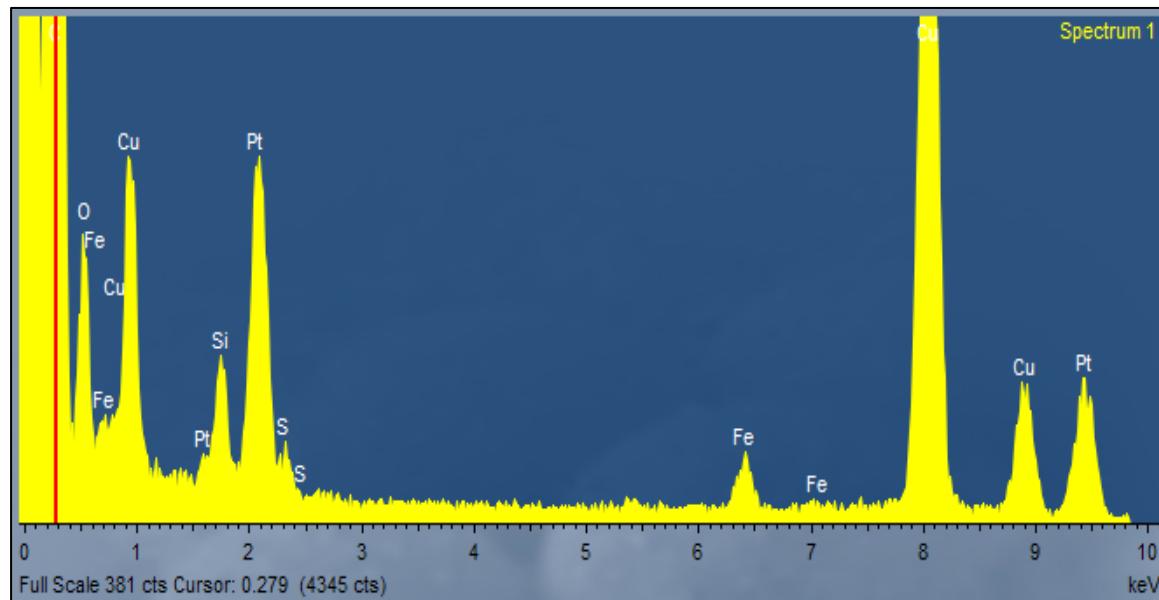


Figure S9. EDX spectra of water soluble FePt nanostars

Element	Peak	Area	k	Abs	Weight%	Weight%	Atomic%
	Area	Sigma	factor	Corrn.		Sigma	
Fe K	830	70	1.170	1.000	21.46	1.75	48.83
Pt L	1372	83	2.592	1.000	78.54	1.75	51.17
Totals					100.00		

Table S9. EDX elemental quantification of water soluble FePt nanostars

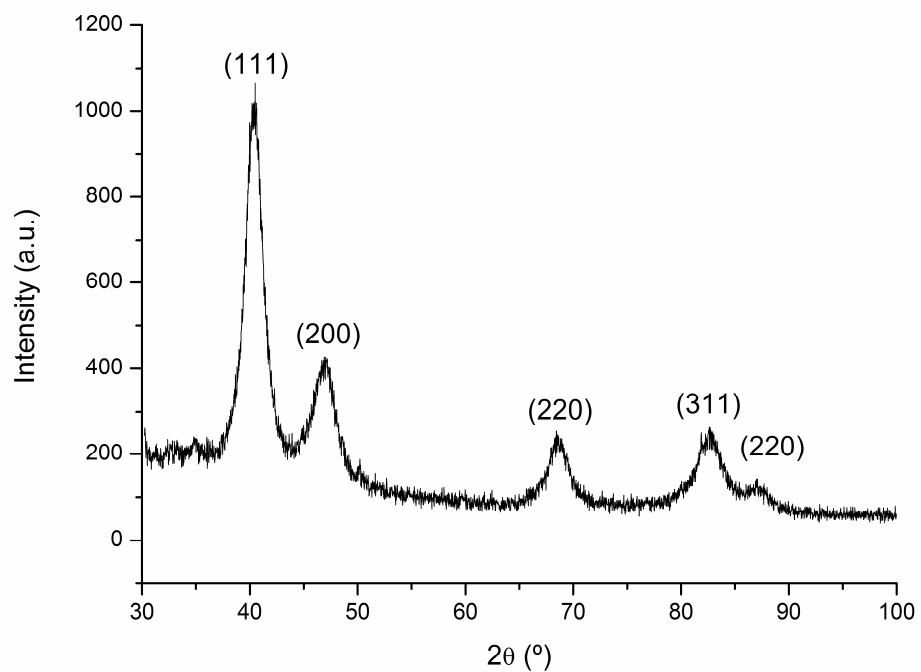


Figure S10. XRD spectra of water soluble FePt nanostars.