

Supporting Information for

Magnetic Actuation of Thermodynamically Stable Dispersion of magnetic nanoparticles in a Liquid Crystal

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1. GENERAL METHODS

Unless stated otherwise, all chemicals were purchased from Sigma-Aldrich and used without purification.

IR spectra were recorded on a FT-IR “Spectrum One” instrument (Italy); samples were deposited from solutions or dispersions on a ZnSe plate and dried prior to analysis. Polarized microscopy was performed using a LOMO “Polam P-111 polarizing microscope equipped with CMOS microscope digital camera “Oplenic Optronics” for imaging with “TSview, version 7.1.1.3” software. TEM was performed on a SELMI PEM-125K instrument. EDS elemental analysis was carried out on a JEOL JSM-6390LV equipped with an X-ray microanalytical system INCA-450. For centrifuging a Sigma 2-11 instrument was used.

Magnetic measurements for the **MNP1** and **MNP2** were performed using a vibration magnetometer. The magneto-optical response of the liquid crystalline materials was studied in the planar cells made from two glass substrates separated by 50 μm polymer strip spacers. The inner surfaces of the substrates were covered with thin ($\approx 0.1 \mu\text{m}$) polyimide layers which were unidirectionally rubbed providing homogeneous planar alignment of the LC along the rubbing direction with a small pretilt ($\approx 1^\circ$). The cells were filled at r.t. by capillary forces.

2. THERMOGRAVIMETRIC ANALYSIS

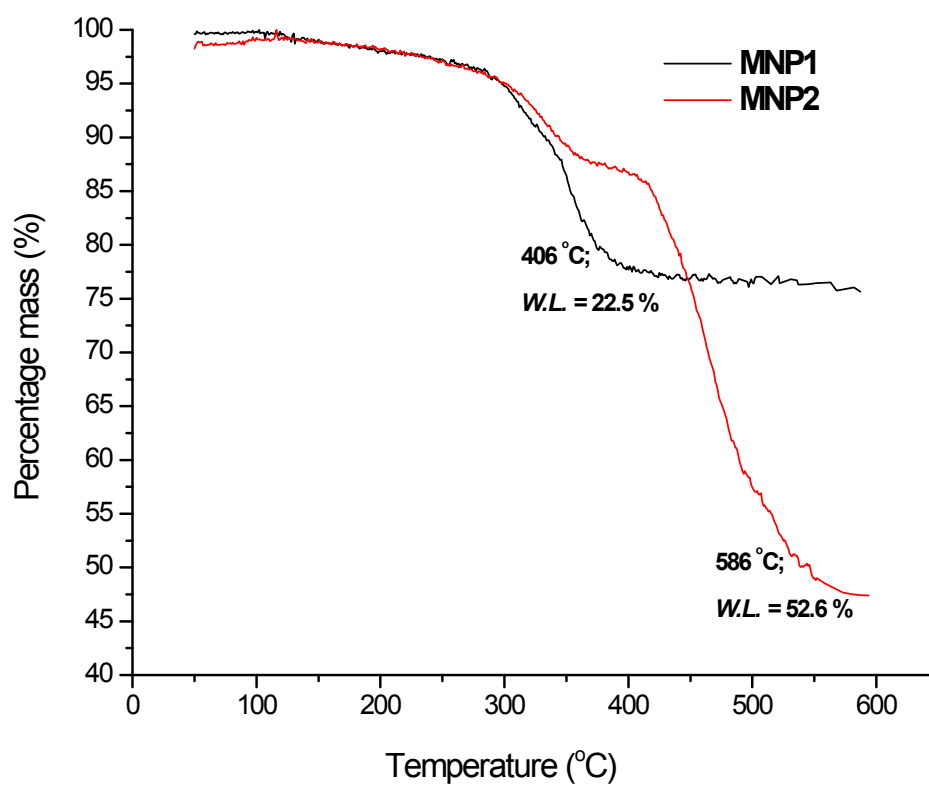


Figure SI-1. TGA plots for starting nanoparticles, **MNP1**, (black curve) and for the modified nanoparticles, **MNP2** (red curve).

3. FT-IR SPECTROSCOPY

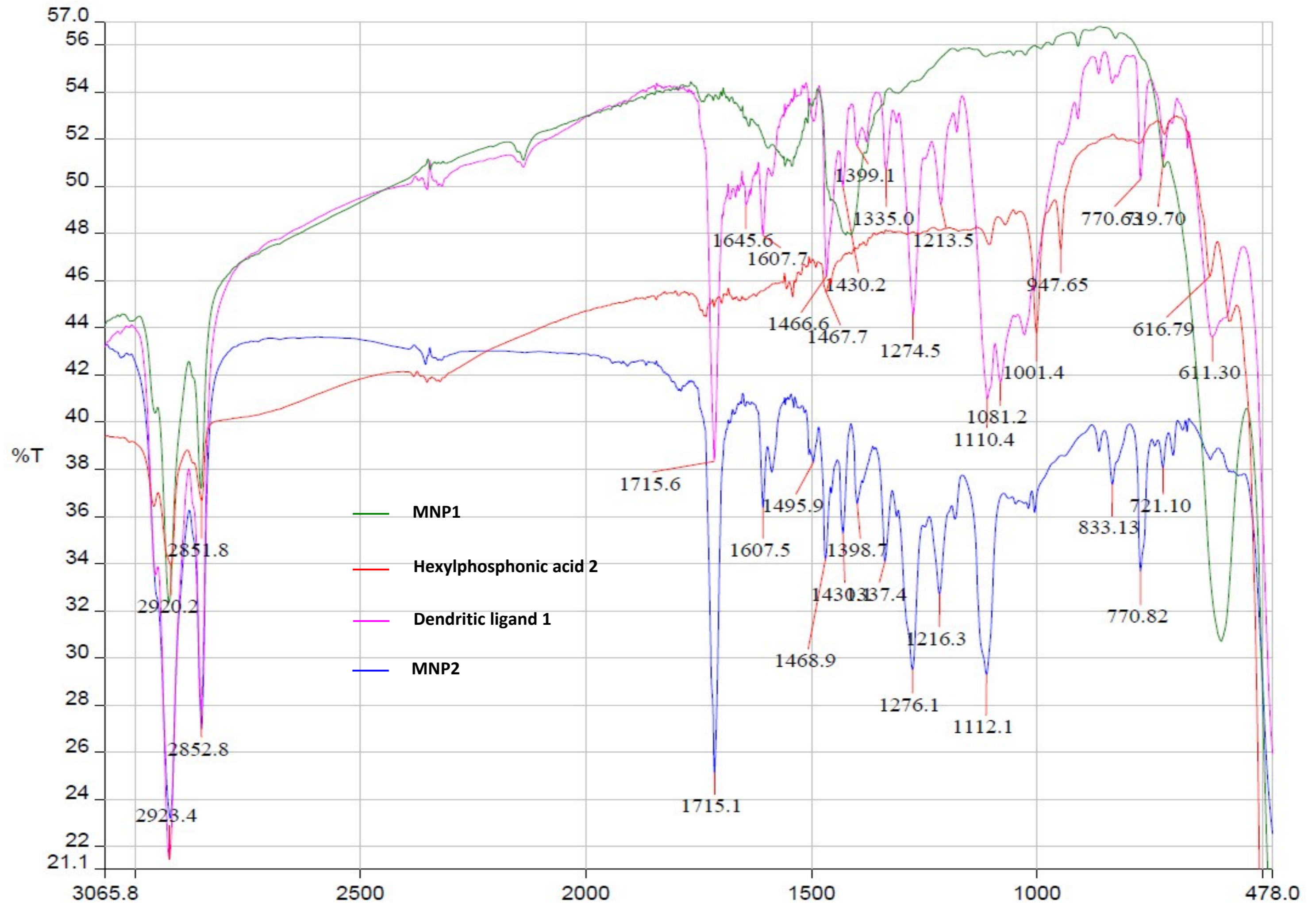


Figure SI-2. FT-IR spectra for CoFe₂O₄ nanoparticles covered with oleic acid/oleylamine (MNP1) (green curve), covered with the mixture of ligands 1 and 2 (MNP2, blue curve), and for pure compounds 1 (pink curve) and 2 (red curve).

4. ELEMENTAL ANALYSIS

Table S-1. Elemental composition according to EDS analysis data for Co₂Fe₂O₄ nanoparticles before and after surface modification (MNP1 and MNP2)

Atom %	Fe	Co	P
MNP1	64.24	35.76	0
MNP2	61.5	31.2	7.3

4.1 Density of the ligands grafting

The evaluation of the surface ligand density is based on an assumption that the P atoms originates only from ligands which have been directly bounded to the NP surface. This assumption is based on the fact that the product was thoroughly washed for removing any unbounded surfactants. The crystallographic cell parameters for CoFe₂O₄ NPs are: formulae units per cell (z) = 8; crystallographic parameters for cubic shpinel cell, $a \sim b \sim c = 8.387 \text{ \AA} = 0.8387 \text{ nm}$, and cell volume 0.590 nm^3 [A.B. Shinde, *International Journal of Innovative Technology and Exploring Engineering*, 2013, **3**, 64].

The evaluation was made according to following.

The amount of facets (N_f) of the cell on the surface of the nanoparticles is approximately:

$$N_f = \frac{4\pi R^2}{a^2} \quad (1)$$

where R is average radius of NP according to TEM, nm; a is crystallographic cell parameter, nm.

The number of metal atoms (N_{Met}) in one nanoparticle is

$$N_{Met} = \frac{V_{NP}}{V_{cell}} 3z = \frac{4\pi R^3 z}{V_{cell}} = 10102 \quad (2)$$

where V_{NP} and V_{cell} are volumes of one NP and crystallographic cell correspondingly; 3 – is number of metal atoms in formulae unit of CoFe₂O₄.

Thus, the amount of P atoms per one NP (N_p) is:

$$N_p = \frac{N_{Met} w_P}{w_{Met}} = 796 \quad (3)$$

where w_P and w_{Met} are atomic percentages of phosphorous and total metal correspondingly, according to EDS data., and surface density of P atoms (SD_P) is estimated to be (spherical approximation):

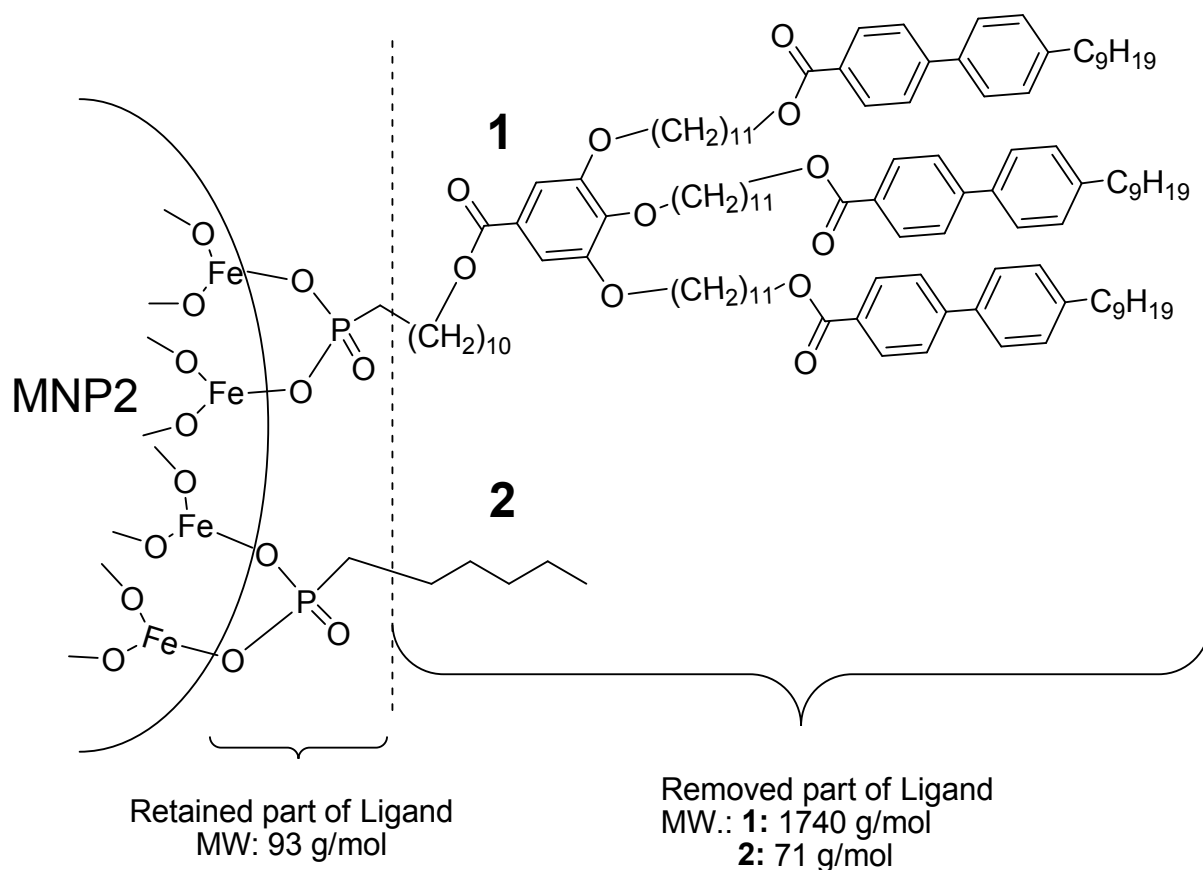
$$SD_P = \frac{N_P}{\pi d^2} = 4.2 \text{ (molecules/nm}^2\text{)} \quad (4)$$

Thus, for 7,3 % of P content we get 796 P atoms per one NP, and approx. 4.2 molecules of ligand per nm².

Calculation of the real ratio of ligands **1** and **2** present at the NPs surface we carried out using following formula [M.V. Limaye, Sh.B. Singh, S.K. Date, D. Kothari, V.R. Reddy, A. Gupta, V. Sathe, R.J. Choudhary, S.K. Kulkarni, *J. Phys. Chem. B*, 2009, **113**, 9070]:

$$N = \frac{w N_A \rho \frac{4}{3} \pi R^3 \times 10^{-23}}{M^{av}_{corr}} \quad (5)$$

where N is number of organic molecules on the NP surface obtained from EDS analysis (796); w – is weight loss according to TGA (see below), %; N_A is Avogadro's number; ρ is density of NP (5.15 g/cm³); R is average radius of NP (3.9 nm according to TEM analysis); M^{av}_{corr} is corrected average molecular weight of organic ligands mixture (g/mol). Correction of the average molecular weight of the ligands was made according the following consideration (see Scheme SI-1) since it is known that in the case of phosphonic acids ligands preferable cleavage of the P–C occurs rather than P–O–Fe bond [C. Yee, G. Kataby, A. Ulman, T. Prozorov, H. White, A. King, M. Rafailovich, J. Sokolov, A. Gedanken, *Langmuir* 1999, **15**, 7111]:



Scheme SI-1

If adopt the proposed mechanism of organic ligand desorption (Scheme SI-1), the corrected average molecular weight of organic ligands mixture obtained from (5) is $M_{corr}^{av}=510$ g/mol. From this the molar fraction of each ligand can be easily calculated solving an equation: where n_1 is molar fraction of ligand **1** at the NPs surface, M_{corr1} and M_{corr2} – corrected molecular weight of ligand **1** and **2** correspondingly (1740 and 71 g/mol).

$$n_1 M_{corr1} + (1 - n_1) M_{corr2} = M_{corr}^{av} \quad (6),$$

Substituting the values into the equation (6) we obtain $n_1 = 0.26$. Therefore the molar fraction of hexylphosphonic acid **2** is $n_2 = 0.74$. These values are very close to the initial ratio of ligands used for the surface modification procedure.

5. TRANSMISSION ELECTRON MICROSCOPY FOR MNP2 COLLOID IN E7

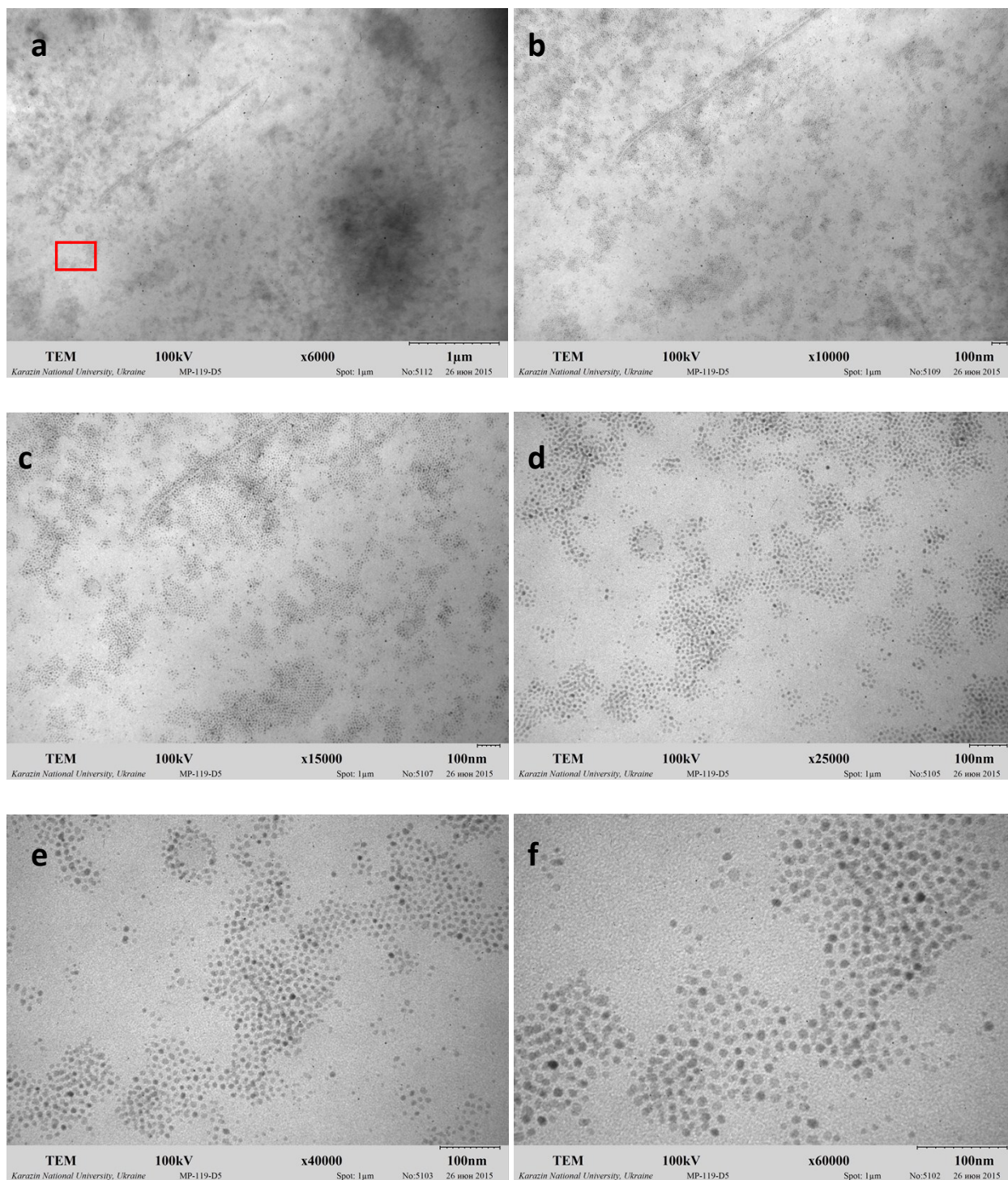


Figure SI-3. TEM images of the 1 wt % dispersions of **MNP2** in E7. Red rectangle shows the magnified area (**a**). Successive zooming of the area marked with a red rectangle (**b-f**).

6. MAGNETIC MEASUREMENTS

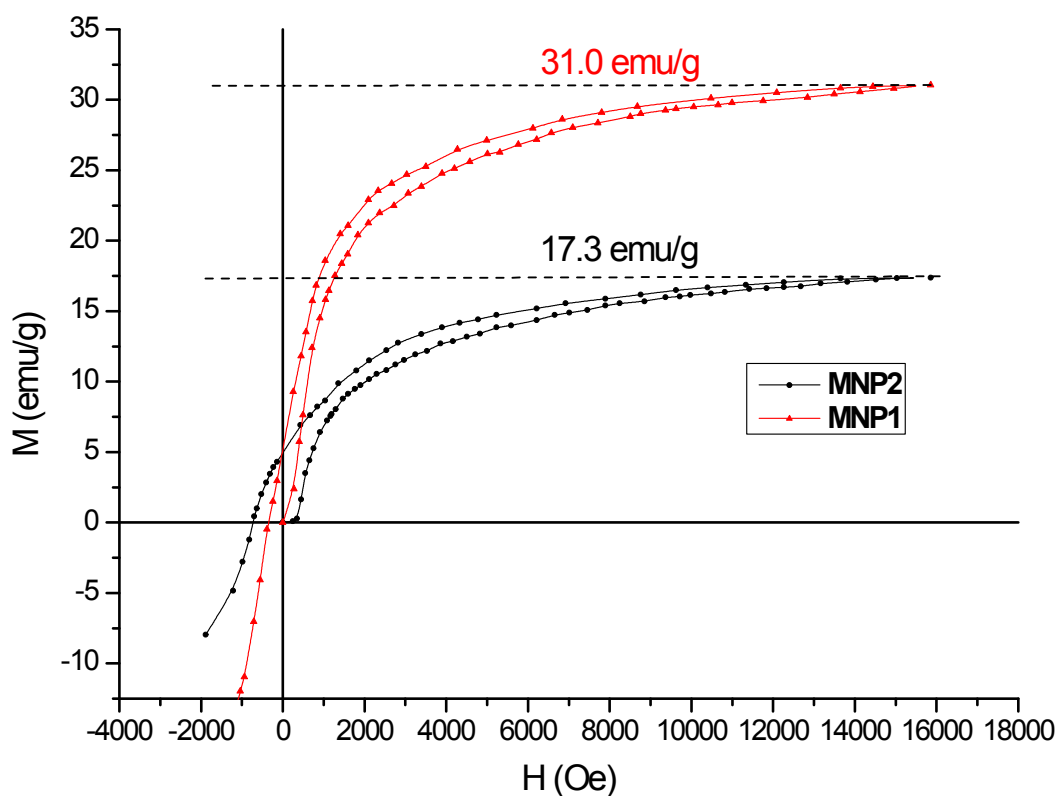


Figure SI-4. Magnetization curves as a function of an applied field for nanoparticles **MNP1** (red curve) and **MNP2** (red curve) at r.t.

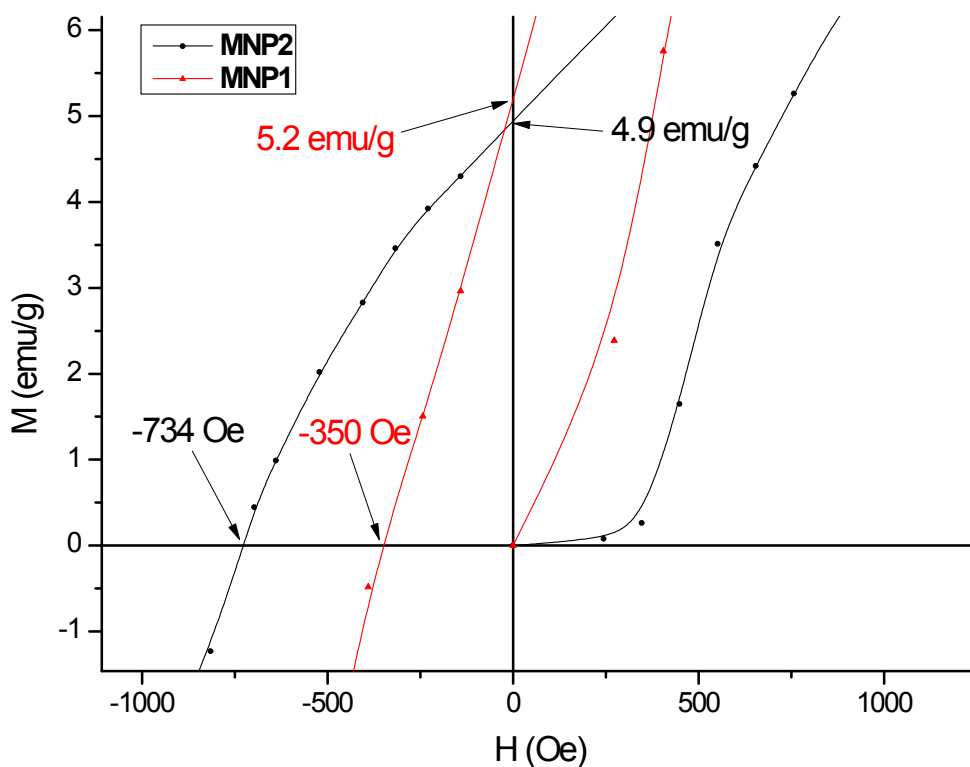


Figure SI-5. Magnified central region of the magnetization curves for nanoparticles **MNP1** (red curve) and **MNP2** (red curve) at r.t.

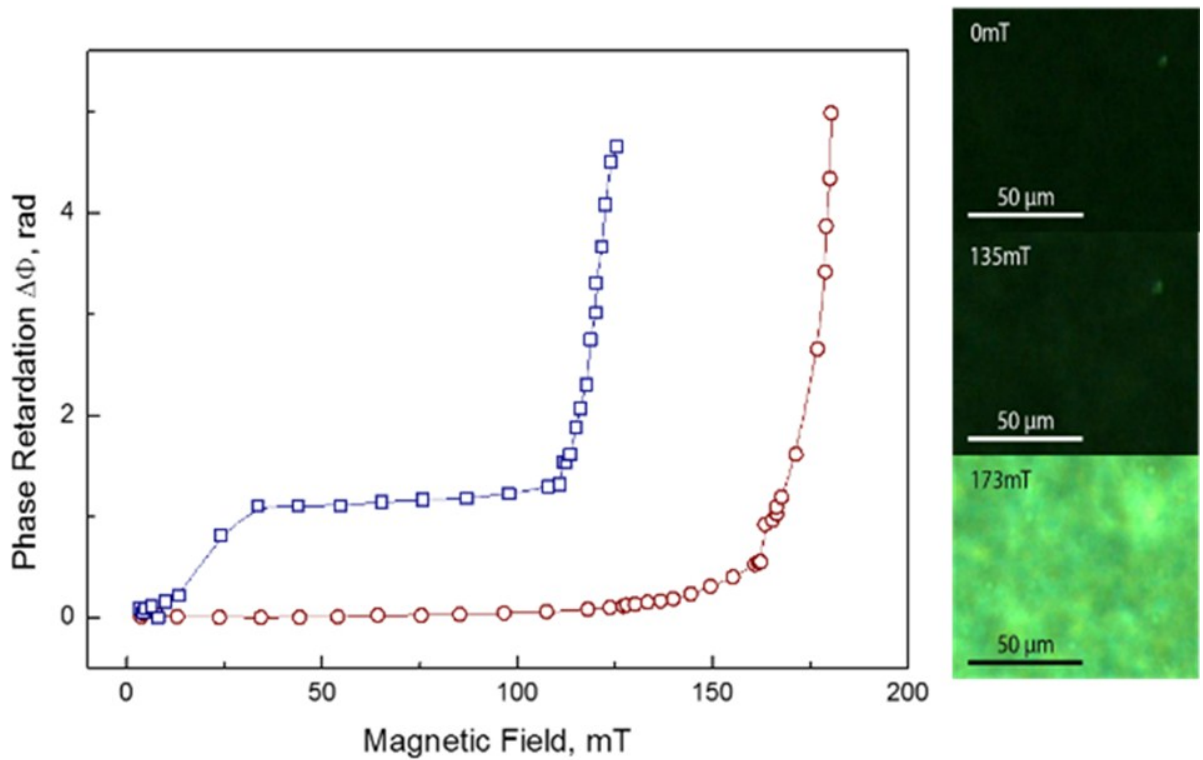


Figure SI-6. The plot: dependencies of the magnetically-induced phase retardation of the suspension (squares) and the individual LC host on the magnetic field. Photos: textures of the pure LC between crossed polarizers at the different values of magnetic field.

7. CALCULATION OF NANOPARTICLES VOLUME FRACTION AND ESTIMATION OF THE AVERAGE DISTANCE BETWEEN NANOPARTICLES FOR THEIR DISPERSIONS IN E7

The volume fraction of MNPs in colloids is useful parameter for estimation of important structural features of colloids, thermodynamical parameters *etc.*, and it can be calculated from mass concentration in several ways. One of them is “geometric” way basing on TEM data and molecular modeling of the surface modifier. Alternatively, the TGA data can be applied for such calculation. In this case mass lost is attributed to organic shell and residual mass is mainly relates to inorganic core.

Application of “geometric” approach

The volume of a spherical MNP (V_{NP}) of diameter $d = 7.8$ nm is given by:

$$V_{NP} = \frac{1}{6} \pi \times d^3 = \frac{1}{6} 3.14 \times 7.8^3 = 248.3 \text{ nm}^3 \quad (1)$$

According to PM3 molecular simulations, the molecular length of surfactant **1** (l) in its most extended conformation is approximately 5.6 nm. Assuming an orthogonal orientation of the surfactant molecules with respect to the NP surface, the total volume of core-shell NP (V_{NP+S}) is therefore given by the equation:

$$V_{NP+S} = \frac{1}{6} \pi (d + 2l)^3 = \frac{1}{6} 3.14 (7.8 + 2 \times 5.6)^3 = 5882 \text{ nm}^3 \quad (2)$$

and the volume of the organic shell (VS) only is given by:

$$V_S = V_{NP+S} - V_{NP} = 5634 \text{ nm}^3 \quad (3)$$

The density of the CoFe_2O_4 core $\rho_{NP} = 5.3 \text{ g cm}^{-3}$. Thus, the mass of the CoFe_2O_4 core is given by:

$$m_{NP} = V_{NP} \times \rho_{NP} = 2.48 \times 10^{-19} \times 5.3 = 1.3 \times 10^{-18} \text{ g} \quad (4)$$

It is reasonable to suppose that the density of the surfactant at the NP surface is close to the density of pure E7 ($\sim 1.0 \text{ g cm}^{-3} = 1 \times 10^{-21} \text{ g nm}^{-3}$). Thus, the organic shell mass is:

$$m_S = V_S \times \rho_S = 5634 \times 10^{-21} = 5.63 \times 10^{-18} \text{ g} \quad (5)$$

And total mass of a NP is:

$$m_{NP+S} = m_{NP} + m_S = 6.93 \times 10^{-18} \text{ g} \quad (6)$$

and average density of the NP with the surfactant shell is 1.18 g cm^{-3} , which is 18% greater than the density of pure E7.

Therefore, 1 g of dispersion with MNPs concentration $C_{NPs} = 1 \text{ wt } \%$ contains $m(NPs) = 0.01 \text{ g}$ of NPs and the following amount of NP (n_{NPs}):

$$n_{NPs}(1\%) = \frac{m(NPs)}{m_{NP+S}} = \frac{0,01}{6.93 \times 10^{-18}} = 1.44 \times 10^{15} \text{ NPs} \quad (7)$$

$$n_{NPs}(5\%) = \frac{m(NPs)}{m_{NP+S}} = \frac{0,05}{6.93 \times 10^{-18}} = 7.20 \times 10^{15} \text{ NPs} \quad (8)$$

And since the density of dispersion is close to that of E7, for uniformly distributed NPs the mean volume of the colloid per particle (V_{per1NP}) is:

$$V_{per1NP}(1\%) = \frac{V_{1g \text{ of dispersion}}}{n_{NPs}} = \frac{1 \times 10^{21}}{1.44 \times 10^{15}} = 6.94 \times 10^5 \text{ nm}^3 \quad (9)$$

$$V_{per1NP}(5\%) = \frac{V_{1g \text{ of dispersion}}}{n_{NPs}} = \frac{1 \times 10^{21}}{7.20 \times 10^{15}} = 1.39 \times 10^5 \text{ nm}^3 \quad (10)$$

The mean distance between centres of NPs ($l_{1\%}$) is proportional to the cube-root of the mean volume per one particle:

$$l_{1\%} = \sqrt[3]{6.94 \times 10^5} = 88.5 \text{ nm} \quad (11)$$

The same calculations for $C_{NPs} = 5 \text{ wt } \%$ result in $l_{5\%} = \mathbf{51.8 \text{ nm}}$.

Taking into account diameters of the NPs including surfactant ($d_{NP+S} = 19 \text{ nm}$) the mean distances between neighbouring MNPs will be approx. **69.5 nm (1% wt colloid)** and **32.8 nm (5% wt colloid)** *i.e.* 3.6 and 1.7 diameters of a NP (with the organic shell) correspondingly.

Thus, the volume fractions of the NPs cores (magnetic material without shell) in LC can be found:

$$f_v(1\%) = \frac{V_{NP}}{V_{per1NP}(1\%)} = \frac{248.3}{6.94 \times 10^5} = 3.6 \times 10^{-4} \text{ nm}^3 \quad (12)$$

$$f_v(5\%) = \frac{V_{NP}}{V_{per1NP}(5\%)} = \frac{248.3}{1.39 \times 10^5} = 1.8 \times 10^{-3} \text{ nm}^3 \quad (13)$$

The same calculations taking into account the NPs organic shell result in the volume fractions:

$$f_{v+s}(1\%) = \frac{V_{NP+S}}{V_{per1NP}(1\%)} = \frac{5882}{6.94 \times 10^5} = 8.5 \times 10^{-3} \text{ nm}^3 \quad (14)$$

$$f_{v+s}(5\%) = \frac{V_{NP+S}}{V_{per1NP}(5\%)} = \frac{5882}{1.39 \times 10^5} = 4.2 \times 10^{-2} \text{ nm}^3 \quad (15)$$

7.1 Application of TGA data

This method is based on the assumption that all loss of the mass under the TGA is related to organic shell, whereas residue is attributed to inorganic core, CoFe_2O_4 in our case. Taking into account the supposed density of organic shell (approx. 1 g cm^{-3}) and inorganic core ($\rho_{NP} = 5.3 \text{ g cm}^{-3}$). see chapter 6.1 above), the volumes of cores (V_{NP}), shells (V_S) and core-shell NPs (V_{NP+S}) as well as average densities (*A.d.*) for nanoparticles **MNP2** and volume fractions in E7 are therefore as following (see Supporting Table 2):

Supporting Table 1. TGA data, volumes of NPs, average density and volume fractions calculated for **MNP2** LC colloids

Wt. conc. MNP2 in E7	<i>W.L.</i> %	V_{NP} , cm^3 *)	V_S , cm^3 *)	V_{NP+S} , cm^3 *)	<i>A. d.</i> , g cm^{-3}	f_v (TGA)	f_{v+s} (TGA)	f_v (Geometric)	f_{v+s} (Geometric)
1%	47,4	0,10	0,474	0,574	1,74	1.0×10^{-3}	5.7×10^{-3}	3.6×10^{-4}	8.5×10^{-3}
5%						5.0×10^{-3}	2.9×10^{-2}	1.8×10^{-3}	4.2×10^{-2}

*) V_{NP} , V_S and V_{NP+S} are calculated for 1 g of NPs concentrate (*i.e.* NPs+organic shell)

As it can be seen from results above, the volume fractions of NPs+Surfactant, estimated using geometric approach, are about 1.4 times higher than that estimated using TGA data. Thus, to our opinion, two these approaches result in estimation of boundary values of volume parts. The “geometric” calculation overrates the volume fraction of the NPs since excluded volume is summarized to the total volume of the NP. Otherwise, the second approach (based on TGA) fully ignores steric factors when surfactant molecules attached to the NP surface *i.e.* all empty places is considered as equally accessible. Additionally, the residual organic impurities left in the NPs shell will increase the “organic” part of the particles.