Clustering in ferronematics—The effect of magnetic collective ordering

Highlights
- Modification of nanoparticle surfaces with specific ligands
- Combined experimental approach reveals structure and magnetization
- Clustering of magnetic nanoparticles in a liquid crystal matrix
- Cluster form dramatically changes collective magnetic properties

Veronika Lacková, Martin A. Schroer, Dirk Honecker, ..., Dmitri I. Svergun, Peter Kopčanský, Natália Tomašovičová

nhudak@saske.sk

Lacková et al., iScience 24, 103493
December 17, 2021 © 2021 The Authors.
https://doi.org/10.1016/j.isci.2021.103493
INTRODUCTION

The revolutionary improvements in nanomaterial preparation and control of properties for nanometer-scale structures enable the development of new products, applications, as well as technologies, e.g., in medical and high-tech devices (Kumar et al., 2013; Jeevanandam et al., 2018; Andrews et al., 2019). Very attractive from the designing point of view as functional nanomaterials, liquid crystal-based nanocomposites can be aligned or reoriented by external stimuli such as temperature, light, magnetic, and/or electric fields. Lately, combining the unique properties of nanoparticles (NPs) with the anisotropy of liquid crystals (LCs) has opened up new opportunities for tuning the properties of LCs for novel materials that contribute to the nanotechnology revolution, mainly in areas such as sensors, nanoscale electronics, electro-optics, optical memories, and display devices (Hegmann et al., 2007; Stamatiou et al., 2012). In 1970, Brochard and de Gennes theoretically predicted interesting ferronematic (FN) properties for ferrofluids of LCs doped with anisotropic magnetic nanoparticles (MNPs) (Brochard and de Gennes, 1970). Since then, the hybridization of LCs and NPs has produced new materials in which the response to external stimuli has been dramatically increased. For instance, a low concentration of ferroelectric NPs in different LC media (Copic et al., 2007; Kaczmarek et al., 2008; Liang et al., 2010; Gupta et al., 2010) enhanced birefringence as well as a larger dielectric anisotropy was observed. Moreover, such suspensions showed a reduced Fréedericksz threshold voltage (Reshetnyak et al., 2006) and faster response time in comparison with pure nematic hosts. Besides, in-plane switching for nematic LC was found to be faster after doping with monolayers of graphene flakes (Basu et al., 2016). A lot of interest has been devoted to carbon nanotubes that have an impact on LCs electro-optical properties (Chen et al., 2007; Basu et al., 2010, 2011; Petrov et al., 2013). Other studies on LC systems doped with quantum dots have shown the possibility to modify the dielectric, electro-optical properties of LCs as well as the pitch of cholesteric LCs (Kumar et al., 2011; Cho et al., 2014; Rodarte et al., 2012, 2014; Patranabish et al., 2021; Han et al., 2021).

In analogy with the aforementioned observations, the question naturally arises, if doping with magnetic particles could lead to unique unexpected global magnetic properties of novel mixed compounds. An exhaustive analysis in this field as well as the deeper understanding of relevant driven mechanisms will
be very valuable owing to the huge application potential of MNPs-doped LCs, e.g., in displays, drug delivery vehicles, sensors, or optical elements as controllable lens and lasing, data storage, medical imaging, and in microwave devices (Bahadur, 1990; Lagerwall and Scalia, 2012; Prakash et al., 2020). Creating such hybrid systems, commonly referred to as ferronematics (FNs), demands for long-term stability, which is achieved for highly diluted systems with rather low concentrations of MNPs (10⁻³ – 10⁻⁴ wt%) (Toth-Katona et al., 2014; Prodanov et al., 2016; Qi et al., 2009). Moreover, size and surface properties of MNPs are essential factors for their stabilization in such hybrid materials (Saliba et al., 2013). Therefore, various surfactants are extensively studied for coating the MNP’s surface to decrease or avoid aggregation of MNPs and improve the long-time stability (Podoliak et al., 2012). Recent studies have elaborated specific surface engineering of MNPs with (pro-) mesogenic ligands to prepare NP-LC hybrids and tuning their compatibility with thermotropic LC hosts (Demortière et al., 2010; Appel et al., 2017; Gdovinová et al., 2017; Hähsler et al., 2021). The stability of colloids crucially determines the structure-property relationships and future applications. In our previous work we have studied the changes in the LC structure of a simple nematic mesogen caused by doping with mesogen-hybridized CoFe₂O₄-MNPs as well as the influence of phase transition on the colloidal stability, especially on the alignment of MNPs (Gdovinová et al., 2017). The choice of this specific MNP was motivated by its wide range of interesting properties like the high chemical stability, mechanical hardness, high coercivity, moderate saturation magnetization, and large magneto-crystalline anisotropy (Hashim et al., 2012; Sanpo et al., 2013; Momin et al., 2015; Sharifi et al., 2012; Hähsler et al., 2020; Zákutná et al., 2020), which allow us to expect an unconventional macroscopic behavior of MNP-doped LCs. Indeed, the obtained results in Gdovinová et al. (2017) showed a rapid change in magnetization for a concentrated FN sample contrary to its diluted counterpart in which the influence of MNPs is negligible in comparison with the undoped LC. The observed different behavior of FN samples based on an identical LC and doped with the same kind of MNPs suggests that it is possible to change the magnetic properties of such hybrid dramatically by changing the weight concentration of MNPs in the LC host. In the present paper, we therefore investigated in detail the response of MNPs-doped nematic LC host (4-n-phenyl-4'-cyanobiphenyl (SCB)) to an applied magnetic field over a wide weight concentration range of MNPs. In order to stabilize the CoFe₂O₄-MNPs (CFO-MNPs) in the LC host, the CFO-MNPs were functionalized with a promesogenic ligand (i.e., [16-(4'-cyano-[1,1'-biphenyl]-3'-4'-yloxy)hexadecanoic acid]) to yield CFO@ligand-MNPs. To perform a systematic analysis the suspensions of SCB doped with CFO@ligand-MNPs were prepared with five different concentrations: LC1, 0.065 wt.%; LC2, 0.082 wt.%; LC3, 0.098 wt.%; LC4, 0.115 wt.%; and LC5, 0.131 wt.%. We observed a non-trivial magnetic behavior. For all FN mixtures, the study combines SQUID magnetometry and complementary capacitance measurements, small-angle X-ray and neutron scattering measurements to investigate the structural transition and alignment of MNPs and LC.

RESULTS AND DISCUSSION

Before a detailed discussion we would like to note that differences in the thermal regime of all used experimental methods (capacitance, SQUID, SANS, and SAXS measurements) do not have any significant impact on the qualitative interpretation of the obtained results. All mentioned measurements were done in nematic state of LC, i.e., below the isotropic-nematic transition temperature. The aforementioned statement is in particular based on the SAXS thermal analysis (exhaustively described in the Supporting Information), where the averaged scattering intensity as well as the orientational order parameter are almost thermally independent for all five investigated samples in the temperature range below 30°C.

Magnetization measurements

The magnetization measurements performed on the SQUID magnetometer are presented in Figure 1. At first, it was necessary to verify the magnetic response of both colloidal components separately to better understand the behavior of their mixture. In accordance with our expectation, the shape of the magnetization curve of CoFe₂O₄-MNPs (CFO-MNPs) powder presented in Figure 1A reflects the magnetic properties of CFO-MNPs with a typical “S” behavior. The size of the MNP-core is below the Shliomis size (Fortin et al., 2007; Hergt et al., 2010) and therefore the magnetic moment relaxes due to Neél relaxation. In Figure 1B the magnetization curve of undoped SCB is given indicating diamagnetic behavior characterized through the linear behavior of magnetization with a negative slope at high-enough amplitude of an external magnetic field.

The most interesting results of our investigation are collected in Figure 2, where the response of MNPs-doped LC on an applied magnetic field is presented for all five concentrations: LC1, 0.065 wt.%; LC2, 0.082 wt.%; LC3, 0.098 wt.%; LC4, 0.115 wt.%; and LC5, 0.131 wt.%. Apparently, the magnetization curve behavior is non-trivial,
the increase of MNPs concentration does not lead to a proportionate increment of the saturation magnetization. For a weak magnetic field (see Figure 2B), the highest magnetic response of analyzed systems is detected for the LC4 compound, whereas the magnetization of the most concentrated sample LC5 is detected significantly below the LC4 and even the LC3 sample. One possible explanation of this unexpected behavior could be a modified total magnetic moment due to the relevant changes of dipolar magnetic interaction among the particles. We suppose that the increasing collinear magnetic interparticle coupling supports the effect of an external magnetic field, resulting in the rapid increment of magnetization in comparison with a disordered system. On the other hand, anticorrelation between neighboring core moments (Bender et al., 2018) hamper an external magnetic field to reorient all magnetic moments in its direction, and thus the final magnetization curve is observed below its paramagnetic counterpart.

For comparison, we calculated the magnetization curves for well dispersed, non-interacting MNP in LC medium, shown in Figure 3. In such colloid, both components, ferromagnetic from MNPs and diamagnetic from LC, contribute to final magnetization (Saari et al., 2015). The comparative analyses of experimental measurement and calculations are shown in Figure 4.

The experimentally measured magnetic moments of the LC2 and LC5 compounds do not achieve the saturation value of their non-interacting counterparts contrary to the sample LC4, where the measured magnetic response is obviously above the theoretical predictions indicating an antiferromagnetic and ferromagnetic type of interaction, respectively. An extreme behavior is detected for the samples LC1 and LC3. LC1 shows a purely dominant diamagnetic contribution of the LC in the final magnetic curve. In contrast to this, the diamagnetic contribution originating from the LC matrix in the LC3 sample is completely reduced and an almost perfect linear character of measured curve is observed in the whole investigated region of an applied electric field. The strong, unexpected deviation of the saturation magnetization of all samples hints to strong connection between MNP aggregates and nematic direction. Strongly anisotropic MNPs structures could potentially overcome entropic effects that usually dominate the orientation behavior of liquid crystals and could be interpreted as an enhancement of a magnetic anisotropy in the sample as a consequence of a strongly anisotropic type of MNPs clusters.

All observations discussed apparently suggest the existence of different types of the magnetic exchange interaction in the colloids under the variation of MNPs concentration. We suppose that the driving mechanism responsible for such unexpected behavior could be found in the formation of different magnetic clusters in CFO-LC at the specific concentration of MNPs (Demortière et al., 2010; Gdovinová et al., 2017). As shown by Clime and Veres (2007), the magnetization of densely packed interacting superparamagnetic nanoparticles assembled into clusters can increase or decrease compared with non-interacting particles, depending on the size and dimensionality of clusters.

**SAXS measurements**

To confirm our hypothesis, we have performed SAXS measurements to determine the structure of MNPs in the FN mixture at T= 40°C. At this temperature, the entire sample is isotropic, and, therefore, the
corresponding 1D curves can be analyzed using standard approaches (Svergun et al., 2013; Li et al., 2016; Schroer and Svergun, 2018). As 5CB is unstructured under these conditions, it can be treated as an additional background contribution and subtracted from the 1D profiles of the mixtures. The corresponding background-corrected SAXS curves for MNPs at the five different concentrations are shown in Figure 5. All curves exhibit similar angular dependency, which can be divided into three regions: at the smallest angles, for \( q < 0.3 \text{ nm}^{-1} \) the data exhibit a power law decay, whereas at wider angles, for \( q > 1.0 \text{ nm}^{-1} \) the profiles point to the presence of smaller particles. In the intermediate transition region, a shoulder due to interparticle correlations between the CFO@ligand-MNPs is observed. In more detail, for \( q > 1.0 \text{ nm}^{-1} \) the absence of any form factor oscillation in the scattering profiles point to the lack of a distinct spherical particle shape and may indicate a polydisperse particle ensemble with size and shape dispersity.

The underlying volume weighted particle size distribution function \( D_{\text{Vol}}(r) \) assuming spherical particles was determined from the outer parts of the SAXS curves (1.0 nm\(^{-1} \) < \( q < 2.5 \text{ nm}^{-1} \)) using the program GNOM (Svergun, 1992). The resulting distributions for all concentrations display a similar bimodal appearance with maxima at \( r \approx 1.7 \) nm and \( r \approx 2.7 \) nm (see Figure 6A). The observed deviations between the distributions are relatively minor and, in particular for \( w = 0.065 \) wt.% (LC1), are likely due to the limited accessible q-range for the determination of the distribution function (see the GNOM fit in Figure 5, which extrapolates the scattering signal to zero angles). The size of the MNPs core is \( d = 3.1(\pm 0.8) \) nm as determined by transmission electron microscopy. As the scattering contrast of the soft and flexible organic shell is much weaker than that of the MNPs, only the core is visible in the SAXS measurement (Schulz et al., 2018).

In the mid-q-range, 0.4 nm\(^{-1} \) < \( q < 1.0 \text{ nm}^{-1} \), there is a strong deviation from the form factor contribution of the small MNPs, indicating the presence of interparticle interference. The rough position of the shoulder at \( q_{\text{corr}} \) is marked in Figure 5. The corresponding correlation length, estimated as \( d_{\text{corr}} = 2\pi / q_{\text{corr}} \approx 7 \) nm, only slightly exceeds the effective particle diameter (SAXS: \( \sim 4–6 \text{ nm} \)) indicating that the particles are in rather close contact and interact with each other.

For \( q < 0.3 \text{ nm}^{-1} \), the SAXS curves follow basically a power law decay, i.e., \( I(q) \sim q^{-p} \) (Figure 5) with the power law exponent \( p = 2.5 \) at \( c = 0.065 \) wt.% and \( p = 2.3 \) for the other concentrations. Such a scattering curve is similar to that from mass-fractals and different from spherical and isometric particles (with \( p = 4 \)) (Beaucage, 1996). Our data therefore point to the presence of reaction-limited clusters formed by the small MNPs in solution. Within these clusters, the MNPs are in close contact. A close inspection of the SAXS curves at small \( q \) actually indicates slight modulations of the power-law decay. In order to extract this additional structural information on the clusters, pair-distance distribution functions \( p(r) \) from the SAXS profiles at very small \( q \) were determined. The results in Figure 6B indicate that the effective size of the clusters is indeed different, with a maximum size of at least \( d_{\text{max}} \approx 190 \) nm. In addition, the related shape of the clusters appears also to be different. Except for \( c = 0.098 \) wt.% (LC3) and, to a much lesser extent for \( c = 0.082 \) wt.% (LC2), the \( p(r) \) functions demonstrate an inverted parabolic profile, typical for a flattened shape of the clusters. The \( p(r) \) for LC3 points to an elongated shape of presented clusters.

Figure 2. The magnetization curves of ferronematics
(A and B) (A) FN mixtures in the nematic phase for five different concentrations of MNPs over the whole investigated region of magnetic field and (B) at a low magnetic field.
In order to obtain tentative shape models of the clusters, ab initio modeling from the SAXS curves at small angles has been performed using the program DAMMIN (Svergun, 1999) of the ATSAS package. Figure 7 depicts the resulting ab initio shape models. As size of the dummy beads used to model the SAXS curves, a radius of 3 nm was chosen, which roughly corresponds to the MNP size. For all five samples, the models exhibit an overall elongated shape for the magnetic clusters. The models can be roughly separated into two classes: LC1, LC4, and LC5 have a more bulky and flat shape, whereas LC2 and, in particular, LC3 are much slimmer. All five models indicate a rather partially branched structure than a well-defined surface, indicative of the aggregation process. Also, all models exhibit an aspect ratio (AR) between 2 and 3. It should be noted that the presented models, owing to the size polydispersity as well as the aggregation process, represent an averaged cluster volume rather than a well-defined shape.

The asymmetric shape of all clusters can alternatively be directly deduced from the anisotropic shape of the 2D SAXS patterns, as is presented for one representative LC4 sample in Figure S1 of supplemental information. The scattering signal at small angles, stemming from the clusters, is aligned with respect to the SCB matrix. In more detail, the short axis of these elongated clusters is pointing toward the LC director, indicating an orientational coupling between the LC matrix and MNP clusters. The different shapes of the clusters are expected to be a consequence of the (de-)aggregation process, which is dependent on the interparticle interactions, particle concentrations, and external perturbations, the last being induced by the dilution process (Mackert et al., 2021). As samples LC1 to LC4 have been prepared by dilution of the LC5 stock solution, the structural difference can be attributed to de- (LC3, LC4) and re-agglomeration (LC1, LC2) of structure LC5. LC4 exhibits a rather slightly different shape, indicative of mild disruptive effects, whereas LC3 appears to be broken up during the dilution process. On further dilution, the shapes become compact again, indicating re-aggregation. Therefore, the LC3 structure appears to reflect a rather stable structure, as further dilution did not result in additional fragmentation. As such a stability is dependent on the specific interactions between the nanoparticles forming the cluster, it appears reasonable that these interactions also have a particular influence on the response to external magnetic fields and thus are the reason for the observed findings.

**SANS measurements**

To provide independent confirmation of the results from the magnetization measurements, SANS measurements of the samples were performed at six different values of magnetic field ($B = 0, 0.05, 0.1, 0.2, 0.5$, and $1$ T). SANS measurements with a polarized neutron beam (SANSPOL) in general allow one to obtain information on the magnetization distribution (Bonini et al., 2007). However, the data show
Figure 4. The comparative analysis of magnetizations curves
Full symbols represent calculated magnetization curves of the non-interacting MNP in LC medium. Open symbols represent measured magnetization of five investigated concentrations. The right panels are the details in the proximity of low magnetic field curves $H<1.5$ kOe.
negligible spin-dependent nuclear-magnetic scattering cross sections in the per mille range compared with the total scattering. This finding is explained by the low volume fraction of MNPs such that the magnetic scattering due to MNPs is superimposed by the strong nuclear scattering of the LC host and the incoherent scattering background due to abundant hydrogen. The further analysis of the LC orientation was performed using the unpolarized SANS data.

For the undoped 5CB, a nearly isotropic scattering pattern is observed at zero applied magnetic field (Figure 8A). With applied magnetic field, one observes a transition to an elongated anisotropy with enhanced scattering along the (horizontal) field direction and reduced intensity in the vertical direction, due to an alignment of anisometric molecules perpendicular to the field; see Figure 8B.
However, for the FN mixtures, the scattering patterns initially show a fully different behavior depending on the MNPs concentration. In accordance with the SQUID measurements, we have identified three types of SANS patterns, collected in the left panel of Figure 9. The first one (Figures 9A and 9C), corresponding to the LC1 and LC2 samples, is characterized by an enhancement of intensity at the left upper and right lower corners, interpreted as magnetic liquid domains oriented perpendicular to each other.

The scattering of LC4 (Figure 9G) is characterized by the initially scattering pattern with the highest intensity in the right upper and left lower corners. The LC3 and LC5 mixtures are (Figures 9E and 9I) characterized by the strong scattering peak at $B = 0$ T, which rotates gradually perpendicular to the applied magnetic field direction (along the $q_x$ vector). Consequently, already the various SANS patterns at $B = 0$ T show that there is a more or less strong prealignment of the LC. Since the external stimulus is identical for all investigated samples, we believe that the MNPs concentration is a crucial mechanism, which forms an initial magnetic arrangement. On analysis of the SANS patterns at non-zero magnetic field (see Figures S8–S12) one identifies different magnetic responses depending on the MNPs concentration. For an illustration see the right panel of Figure 9, which represents the SANS patterns at $B = 0.1$ T. It is clearly evident that the most anisotropic SANS intensity at $B = 0.1$ T corresponds to the LC3 sample, which hints to the larger magnetic

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**Figure 7. Shape models of the clusters determined from the SAXS curves**

Within the SCB matrix, the clusters are aligned such that their long axis are perpendicular to the nematic director. Given are also the average dimensions and the aspect ratio (AR).

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**Figure 8. Two-dimensional SANS patterns**

SCB without applied magnetic field and with $B = 1$ T at room temperature ($T = 25^\circ$C). The magnetic field is oriented horizontal parallel to the $q_x$ axis.

See also Figures S8–S12.
Figure 9. SANS scattering patterns measured at $B = 0 \, T$ and $B = 0.1 \, T$

(A and B) LC1.
(C and D) LC2.
(E and F) LC3.
(G and H) LC4.
(I and J) LC5.
susceptibility of the LC composite. In addition, the transition fields above which the scattering pattern is oriented along the vertical field varies with the MNPs concentration as a consequence of different correlations between magnetic particles and their response to magnetic field, and interactions of the MNP within the LC matrix. One observes for LC1 and LC3 a strong variation with moderate magnetic field of 0.1 T. For LC1, the scattering pattern indicates an almost aligned state, whereas for LC3 the system is still reorienting coherently at an intermediate orientation. For the other concentrations the onset of reorientation happens at fields of 0.2 T for LC2 and even larger for the other compositions. Two-dimensional SANS scattering patterns indicate that the fully polarized state is achieved more easily in the LC mixture with “more isotropic” magnetic clusters, instead of the highly anisotropic shape of the one observed, e.g., in the LC3 phase. For LC3, the scattering patterns at non-zero magnetic field indicate that the director rotates coherently for the whole sample (Figure S10 in the supplemental information). The other mixtures show a redistribution of scattering intensity that is along the field direction toward the edges of the detector for intermediate fields at 0.05–0.1 T caused by the rotation of tilted twin domains.

Capacitance measurements

Finally, we have analyzed the influence of MNPs clustering on the magnetic Fréedericksz transition. Figure 10 shows the capacitance measurements up to 1.2 T with magnetic field dependence of the reduced capacitance $(C - C_0)/C_0$ for undoped LC 5CB as well as for FN samples with different CFO@ligand-MNPs concentrations. Here $C$ and $C_0$ correspond to the capacitances at the actual field and at $B = 0$ T, respectively. For the doped systems, the sensitivity increases with increasing dopant concentration, demonstrating that the magnetic Fréedericksz transition threshold is shifted toward lower fields, and thus from the application perspective gives an opportunity to prepare low-energy-consuming materials for FN applications. However, with increasing concentration of NPs in the composites, we would expect a monotonic decrease of the Fréedericksz transition threshold provoked by the magnetic field, but the obtained results show a non-monotonic behavior. Similarly as in the previous discussion, the concentration and arrangement of MNPs dopants and their properties (e.g., the shape and the effective size of magnetic clusters and/or the type of exchange interaction) have a non-negligible impact on the occurrence of the Fréedericksz transition threshold. It can be attributed to a strong magneto-nematic coupling in the system by choosing appropriate surface-attached MNPs to nematic media.

In conclusion, combining capacitance, magnetization, and SAXS and SANS measurements we present a description of composites made of cobalt ferrite NPs in the nematic LC host 5CB. The magnetic-field magnetization measurements of five concentration compounds (between 0.065 and 0.131 wt.%) performed on the SQUID magnetometer reveal the peculiar and unexpected behavior with a non-proportional enhancement of magnetization with MNPs concentration in colloid. Surprisingly, we identified the huge magnetic response at the MNPs concentration of 0.098 wt.%, in which the diamagnetic contribution is completely absent in the range of investigated magnetic field. On the other hand, the magnetic response

Figure 10. Magnetic Fréedericksz transition
Dependence of the capacitance of the LC 5CB and of the FNs on the applied magnetic field. Inset shows low field region.
of the highest concentrated sample studied (0.131 wt.%) in a low-enough magnetic field is significantly smaller in comparison with other investigated concentrations. Based on the comparative analysis of the measured magnetization curves and theoretically predicted behavior of non-interacting MNPs in LC medium, we suppose that such unexpected observation of magnetic behavior relates to the dramatic changes of the effective correlation inside the LC suspension. For concentrations where the measured magnetization curves are above (below) the theoretical predictions, ferromagnetic (antiferromagnetic) correlation support (reduce) the effect of an external magnetic field. In accordance with this prediction, a high-enough effective correlation can completely overcome the diamagnetic contribution as is observed for LC3. On the contrary, effectively non-magnetic clusters cannot generate a sufficient magnetic response and, thus, the solely diamagnetic contribution is measured. The field-dependent SANS measurements from 0 to 1 T support our hypothesis. Already the 2D SANS patterns show for the MNP concentrations that different field strengths induce a transition from the initial orientation to the field-aligned state. In particular for LC3 a strong scattering anisotropy associated to enhanced orientational order is observed, in good correspondence with the outstanding magnetic response of this sample. It should be emphasized that the initial scattering patterns \( (B = 0 \text{ T}) \) of all five analyzed samples do not coincide as a result of different spontaneous structural arrangements of the LC host. The obtained results suggest that variation of MNPs in the LC host can lead to the cluster formation, the size and dimensionality of which have an impact on global magnetic properties. Finally, from the SAXS we identified the presence of clusters in each analyzed sample. The morphology of these clusters is similar to mass-fractals formed by reaction-limited elongated clusters with an aspect ratio between 2 and 3. We demonstrate that the MNPs clusters induce a ferronematic response of the liquid crystal matrix with a rich concentration dependence. The clusters are coupled with the SCB matrix. Within the nematic phase, the short axis is oriented toward the SCB director.

Limitations of the study
Although our study, combing several experimental methods, revealed that the presence of clusters can create new types of hybrid material with new physical properties, the full mechanisms on the microscopic scale are not yet fully clear. Therefore, we expect our results will stimulate future experimental and theoretical work to reveal the underlying molecular mechanisms in detail. Further research will elucidate the way for fabricating stable ferronematics with tunable magnetic properties suitable for application such as magnetic field sensors or magneto-optical devices.

SUPPORTING CITATIONS
The following references appear in the supplemental information: Davidson et al. (1995); Lorenz et al., (2012); Silva et al., (2015).

STAR METHODS
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SUPPLEMENTAL INFORMATION
Supplemental information can be found online at https://doi.org/10.1016/j.isci.2021.103493.
ACKNOWLEDGMENTS
The authors thank the support by the Slovak Academy of Sciences, in the framework of projects VEGA 2/0043/21 and VEGA 1/0105/20, the Slovak Research and Development Agency under the contract No. APVV-015-0453, MODEx (ITMS2014+: 313011T548) supported by the Operational Programme Integrated Infrastructure (OPII) funded by the ERDF and COST action CA15119 Nanoutake. We gratefully acknowledge the financial support and provision of beam time at the instrument D33 at the Institut Laue-Langevin, Grenoble, France project No. 9-11-1883. M.A.S. and D.I.S. acknowledge the Roentgen-Angstrom cluster project “TT-SAS” (BMBF project number 05K11YEAA) for financial support. S.B. and M.H. thank the German Science Foundation (DFG) for financial support within the Priority Program (SPP1681) “Field controlled particle matrix interactions. Synthesis, multiscale modeling, and application of magnetic hybrid materials” (project BE 2243/2-3).

AUTHOR CONTRIBUTIONS
V.L. conceptualization, investigation, writing draft; M.A.S. and D.I.S. SAXS investigation; D.H. SANS investigation; J.K. magnetic properties investigation; P.K. funding acquisition; N.T. supervision; M.A.S., N.T., and V.L. conceptualization, investigation, writing draft; M.A.S. and D.I.S. SAXS investigation; D.H. SANS investigation; M.H. synthesis of samples; H.V. validation; K.Z. visualization; S.B. conceptualization of sample synthesis, multiscale modeling, and application of magnetic hybrid materials.

DECLARATION OF INTERESTS
The authors declare no competing interests.

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STAR METHODS

KEY RESOURCES TABLE

| REAGENT or RESOURCE | SOURCE | IDENTIFIER |
|---------------------|--------|------------|
| **Chemicals**       |        |            |
| 16-Bromohexadecanoic acid (≥ 99%) | Sigma-Aldrich | CAS: 2536-35-8 |
| NaH (suspension 60% in paraffin oil) | Sigma-Aldrich | CAS: 7646-69-7 |
| Tetrabutylammonium hydrogen sulfate (97%) | Alfa Aesar | CAS: 32,503-27-8 |
| 4-Cyano-4’-pentylbiphenyl (99%), | Alfa Aesar | CAS: 40,817-08-1 |
| 4-Hydroxy-4-biphenylcarbonitrile (99%) | Alfa Aesar | CAS: 19,812-93-2 |
| Iron(II)chloride (reagent grade) | Sigma-Aldrich | CAS: 7705-08-0 |
| Cobalt(II)chloride hexahydrate (≥ 99%) | Carl Roth | CAS: 7791-13-1 |
| **Software and algorithms** | | |
| SAXS: ATSAS software | https://www.embl-hamburg.de/biosaxs/software.html | Version 3.0.3 |
| MATLAB | MathWorks | Version R2019a |

RESOURCE AVAILABILITY

Lead contact
Further information and requests for resources and reagents should be directed to and will be fulfilled by the lead contact, Natália Tomášovcová (nhudak@saske.sk).

Materials availability
Materials may be provided upon reasonable request for a specific purpose.

Data and code availability
- The published article includes all data analyzed during this study.
- No original code was generated in the present study.
- Any additional information required to reanalyze the data reported in this paper is available from the lead contact upon request.

METHOD DETAILS

Synthesis of electrostatically stabilized CFO-MNPs
Electrostatically stabilized CoFe_{2-x}O_4 MNPs were synthesized following a modified procedure (Appel et al., 2017). Briefly, a mixture of FeCl_3 (2 mL, 2 M in water) and CoCl_2 (1 mL, 2 M in 3 M hydrochloric acid) was injected (~1 s) into a NaOH solution (80 mL, 1 M) at 50°C while stirring. Then, the reaction mixture was heated to 100°C (heating rate ~5°C/min). After 30 min the MNPs were collected by centrifugation and washed three-times with water. Then, perchloric acid (5 mL, 1 M in water) was added and aggregates were removed by centrifugation to give MNPs as an electrostatically stabilized brown-black colloidal suspension. The composition of the MNPs was determined as CoFe_{2-x}O_4 (x = 0.6) by atomic emission spectrometry with inductively coupled plasma (ICP-OES). The particle size was determined by transmission electron microscopy (TEM). For this purpose, N = 300 MNPs were accounted with an average particle size for the magnetic core of d = 3.1 (±0.8) nm.

Synthesis of CFO@ligand-MNPs via direct functionalization
First, the (pro)mesogenic ligand [16-((4’-cyano-[1,1’-biphenyl]-4-yl)oxy)hexadecanoic acid] was synthesized (Appel et al., 2017). Then, the (pro)mesogenic ligand (200 mg, 0.4 mmol) was dissolved in anhydrous dimethylformamide (30 mL) at 40°C. The MNPs (830 μL MNPs in 1 M perchloric acid) were added and the reaction mixture was stirred at 60°C. After 3.5 h, CFO@ligand-MNPs were precipitated by addition of EtOH (20 mL), washed with EtOH (3 × 20 mL) and eventually magnetically separated.
Preparation of FN mixtures: Doping 5CB with CFO@ligand-MNPs

The CFO@ligand-MNPs were dispersed in 5CB (10 mL) with an ultrasonic probe at 40°C. After transition to the nematic phase, macroscopic precipitates were removed by magnetic separation (25°C, 16 h). A colloidal stable suspension was obtained with 0.131 wt.% CFO in 5CB. The FN mixture was diluted with 5CB to prepare a series of five samples with different CFO@ligand-MNPs concentration: LC1) 0.065 wt.%; LC2) 0.082 wt.%; LC3) 0.098 wt.%; LC4) 0.115 wt.% and LC5) 0.131 wt.% (stock solution).

Magnetisation measurements

The magnetic properties of the 5CB and FNs mixtures were measured using an SQUID magnetometer (Quantum Design MPMS 5XL). The samples were filled into cylindrical capsules, which were hermetically closed. The diameter of the capsules was 2.5 mm and length was 6.5 mm. A diamagnetic signal coming from the container was subtracted after each measurement. The measurement of magnetisation curves was performed at 295 K (~22°C) in the nematic phase.

Small angle X-ray scattering

Small angle X-ray scattering (SAXS) measurements were performed at the BioSAXS beamline P12, EMBL/DESY, Hamburg, Germany (Blanchet et al., 2015), using the 150 μm (V) × 250 μm (H) X-ray beam with an energy of E = 10 keV (wavelength λ = 0.124 nm). Two-dimensional SAXS patterns were recorded using a Pilatus 6M pixel detector (Kraft et al., 2009), at a sample-detector-distance of 3 m, covering the range of momentum transfer q = 0.04–7.3 nm⁻¹ (q = 4π/λsin(θ)), where 2θ is the scattering angle. The samples were filled into quartz glass capillaries (Hilgenberg, Germany; outer diameter: 1.50 mm, wall thickness: 0.01 mm) and placed within a custom-made temperature controlled capillary holder with a Peltier element. Temperature-dependent measurements were performed in the range from T = 20°C to 40°C with 1°C step to monitor the thermally driven transition from the nematic to the isotropic phase of the FNs. Afterward, samples were cooled down back to 20°C. For the samples within the isotropic phase, there is no preferred orientation and the SAXS patterns were azimuthally averaged and normalized by the P12 beamline SASFLOW pipeline (Franke et al., 2012). From these 1D-SAXS curves the background signal from water was subtracted and the difference profiles were further analyzed using the ATSAS software package (Franke et al., 2017).

Small angle neutron scattering

Magnetic-field dependent small-angle neutron scattering (SANS) were performed on D33 at the Institut Laue-Langevin, Grenoble, France (Lacková et al., 2018; Dewhurst et al., 2016) using a neutron wavelength of 3.5 Å(λ = 15%). The two-dimensional SANS was recorded for two instrument configurations with sample-to-detector distances of 2 m and 12.8 m and similar collimation setting (2.8 m and 12.8 m), respectively, which allowed to cover a range of q comparable to the SAXS measurements (0.08–6.2 nm⁻¹) (Lacková et al., 2018). The rear detector captures the data at small momentum transfer q, while the scattering at extended high q were accessible with the surrounding panels of the front detector on D33. A gap in q-coverage around 3 nm⁻¹ occurs due to a lateral offset of the panels from the main detector (Dewhurst et al., 2016). The samples were filled in rectangular quartz cells with a path length of 2 mm and placed inside an electromagnet, which provided a magnetic field of up to 1 T. Finally, all measurements have been performed at temperature of 25°C.

Dielectric measurements

Structural transitions of FNs were monitored by capacitance measurements, where samples were introduced by capillary action into about D = 50 μm thick sandwich cells (MUT, Poland) (0.5 cm × 0.5 cm) made of indium-tin-oxide (ITO) coated glass electrode. The initial alignment of LC molecules was planar, i.e. the director n was parallel to the capacitor electrodes. The capacitor has been placed into a thermostat system, regulated with the temperature stability of 0.05°C, and the measurements have been done at the temperature of 30°C. The capacitance C was measured at the frequency of 1 kHz by a high precision capacitance bridge (Andeen Hagerling, USA) with an accuracy of 0.8 aF at 1 kHz. The magnetic field was applied perpendicular with the initial director orientation n. In this geometry, the magnetic field destabilizes the initial director orientation. Therefore, it is possible to determine the threshold behavior in the re-orientational response of LCs or FNs.