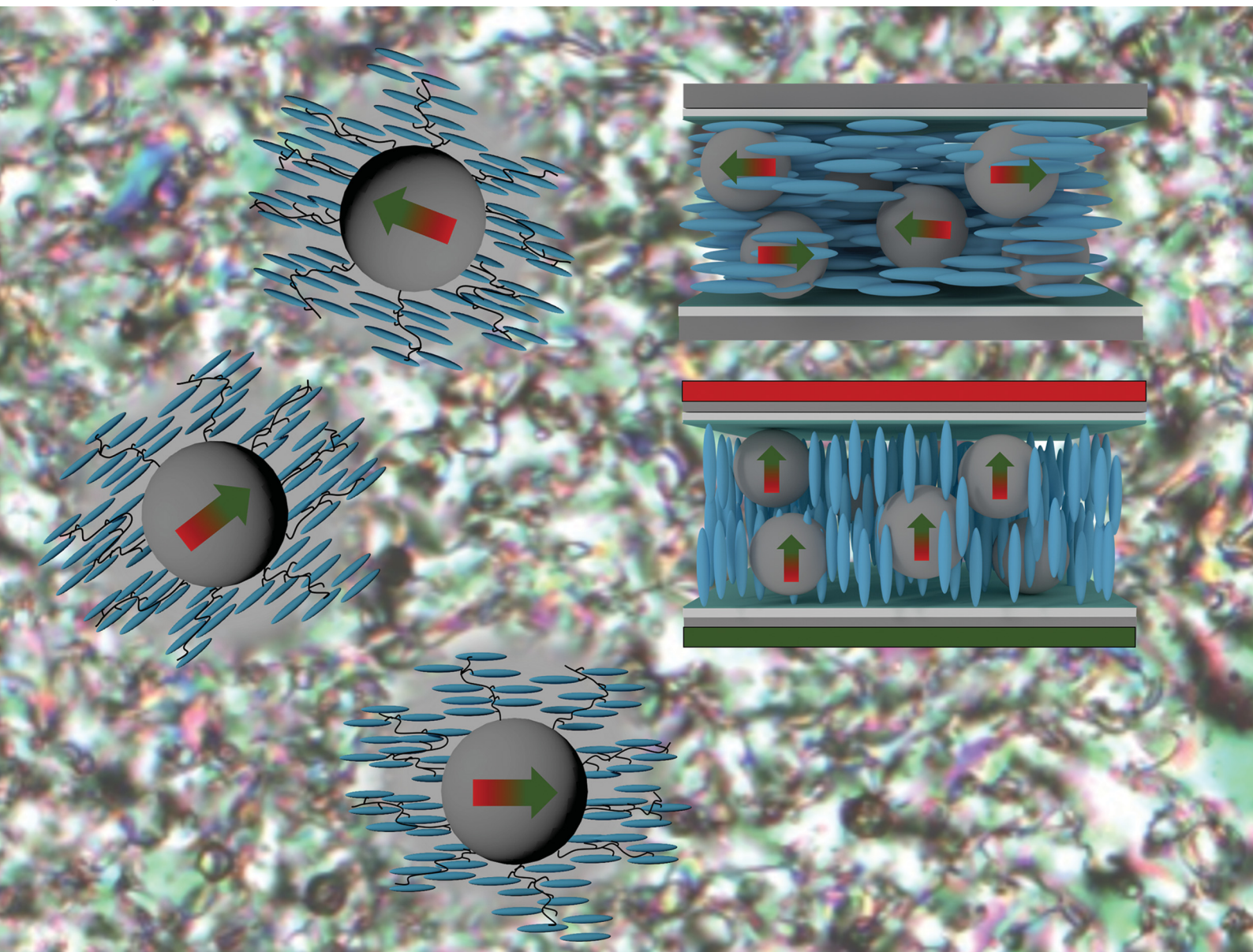


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**PAPER**

Annette M. Schmidt *et al.*  
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# Superparamagnetic nanoparticles with LC polymer brush shell as efficient dopants for ferronematic phases†

Karin Koch,<sup>a</sup> Matthias Kundt,<sup>a</sup> Anda Barkane,<sup>a</sup> Hajnalka Nadasi,<sup>b</sup> Samira Webers,<sup>c</sup> Joachim Landers,<sup>c</sup> Heiko Wende,<sup>c</sup> Alexey Eremin<sup>b</sup> and Annette M. Schmidt<sup>ib</sup>\*<sup>a</sup>

Liquid crystal (LC) based magnetic materials consisting of LC hosts doped with functional magnetic nanoparticles enable optical switching of the mesogens at moderate magnetic field strengths and thereby open the pathway for the design of novel smart devices. A promising route for the fabrication of stable ferronematic phases is the attachment of a covalently bound LC polymer shell onto the surface of nanoparticles. With this approach, ferronematic phases based on magnetically blocked particles and the commercial LC 4-cyano-4'-pentylbiphenyl (5CB) liquid crystal were shown to have a sufficient magnetic sensitivity, but the mechanism of the magneto–nematic coupling is unidentified. To get deeper insight into the coupling modes present in these systems, we prepared ferronematic materials based on superparamagnetic particles, which respond to external fields with internal magnetic realignment instead of mechanical rotation. This aims at clarifying whether the hard coupling of the magnetization to the particle's orientation (magnetic blocking) is a necessary component of the magnetization–nematic director coupling mechanism. We herein report the fabrication of a ferronematic phase consisting of surface-functionalized superparamagnetic Fe<sub>3</sub>O<sub>4</sub> particles and 5CB. We characterize the phase behavior and investigate the magneto–optical properties of the new ferronematic phase and compare it to the ferronematic system containing magnetically blocked CoFe<sub>2</sub>O<sub>4</sub> particles to get information about the origin of the magneto–nematic coupling.

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## Introduction

Liquid crystals (LC) attract considerable interest in science and technology due to the combination of fluidity of liquids with anisotropic optical and mechanical properties as usually found in crystalline solids.<sup>1,2</sup> The anisotropies of the dielectric permittivity ( $\Delta\epsilon$ ) and diamagnetic susceptibility ( $\Delta\chi$ ) allow the alignment of the LC director using external stimuli such as electric voltage or magnetic fields and is essential for their application in optical devices.<sup>1–8</sup> While electric fields are commonly used for such devices over a few decades now, the employment of magnetic fields is less straightforward due to

the low magnetic anisotropy of the mesogens requiring relatively high magnetic field strengths. A way to enhance the magnetic response has been developed in the 70s by De Gennes and Brochard. They proposed that doping LC phases with dipolar magnetic nanoparticles (NP) would result in a coupling between the nematic phase and the magnetic particle that enhances the magnetic sensitivity.<sup>9</sup> Further quantitative predictions on the effective orientation coupling of the Brochard–de-Gennes theory were derived by Burylov and Raikher.<sup>10</sup>

In the meantime, several potentially ferronematic systems containing spherical and anisotropic magnetic nanoparticles have been discovered and investigated in detail, but the ferro-nematic coupling is poorly understood.<sup>11–36</sup> It became obvious, though, that one of the main obstacles for the realization of a stable ferronematic phase are the strong intermolecular interactions of the mesogens on the one hand, in combination with the strong tendency for agglomeration for the magnetic dopants, on the other hand, prohibiting a stable dispersion in many cases.<sup>37</sup> Strategies for the improvement of the compatibility between nanoparticles and the nematic environment are mainly based on utilization of surfactants (*e.g.* oleic acid) or

<sup>a</sup> Universität zu Köln, Department Chemie, Institut für Physikalische Chemie, Luxemburger Str. 116, D-50939 Köln, Germany.  
E-mail: annette.schmidt@uni-koeln.de

<sup>b</sup> Otto-von-Guericke-Universität Magdeburg, Institut für Physik, Universitätsplatz 2, D-39016 Magdeburg, Germany

<sup>c</sup> Faculty of Physics and Center for Nanointegration Duisburg-Essen (CENIDE), Universität Duisburg-Essen, Duisburg, Germany

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surface ligands containing mesogenic units, as they exhibit a high chemical compatibility with the employed LC host.<sup>13,18,34,36,38–40</sup>

In our recent work, we reported a successful fabrication of magnetically blocked  $\text{CoFe}_2\text{O}_4$  particles modified with covalently attached mesogenic polymers as doping agents for stable ferronematic systems/dispersions with an enhanced compatibility and magnetic sensitivity.<sup>21</sup> We show, that the LC polymer brush effectively promotes the interaction between the magnetic dopants and the LC matrix resulting in a material with novel magneto-optical properties. Additionally, we achieved a quantitative description of the data and determined the surface coupling strength in these systems based on free energy considerations.

From early theoretical predictions of the phenomenon,<sup>9,10,41,42</sup> a significant direct magneto–nematic coupling effect between the individual mesogenic molecule orientation and the magnetic stray field of a single magnetic particle is not expected. The exchange energy induced by the magnetic field in the environment of a particle in the respective size range is far lower than  $k_B T$  and thus readily compensated by thermal motion. Instead, the interactions occur by means of a preferential surface alignment of the mesogens with respect to the surface of a magnetic object. If the latter is geometrically anisotropic (non-spherical), this might lead to a preferential orientation of the particle within the nematic matrix, and the reorientation results in the respective co-alignment of the surrounding mesogens. The magneto–nematic coupling is thus justified by a mechanical or orientational coupling based on a strong anchoring of the LC host molecules with the surface of the NP.<sup>9,10,41,42</sup>

However, in systems where spherical magnetic nanoparticles are used as dopants, the surface coupling alone does not explain their enhanced magnetic response, as no preferred direction of alignment is induced by a sphere – instead, dependent on their size, spherical nanoparticles usually represent dipolar two-point defects in the nematic phase, where the two disclination points face each other at the surface of the sphere.<sup>9,22,43</sup> One feasible explanation could be that under field influence, the magnetic nanoparticles form small anisotropic assemblies, *e.g.* chains, that play the role of the directing object.<sup>12,27,44</sup>

In our recent work, the question of the coupling mechanism remained open despite the good quantitative description based on the available theories. However, we suggested the strong enhancement in the experimentally observed magneto–nematic

coupling to two main differences between the systems employed in our study as compared to others:

- Excellent compatibilization and colloidal stabilization of the magnetic nanoparticles with their environment by covalent attachment of a mesogen-functionalized polymer brush shell. It can be assumed that the incorporation of surface-attached LC polymer brushes modifies fundamentally the interactions between the dopant surface and the surrounding nematic phase.

- Employment of magnetically blocked cobalt ferrite particles. Their response to a magnetic field occurs thus by mechanical rotation (Brown relaxation, Fig. 1a), which might be relevant.

It is the goal of the present study to shed more light on this open question of the coupling mechanism by extending the experiments to otherwise similar, but superparamagnetic particles. Due to their low thermal magnetization reversal barrier, the magnetic moments fluctuate with such fast relaxation times, so that no significant field is expected in the absence of an external field, and thus the relevance of this point is lighted up. Moreover, in an applied external field, the particles do not respond by mechanical rotation, but by relaxation of the magnetic moment of the particle with respect to the crystal lattice (Néel relaxation, Fig. 1b). We thus herein report a ferronematic system based on superparamagnetic  $\text{Fe}_3\text{O}_4$  particles with the size, surface functionalization and the magnetic moment comparable with the magnetically blocked particles utilized in our previous work. We explore the magneto-optical behavior of the new ferronematic and compare it to the previous results for more insight into the origin of the magneto–nematic coupling. In addition, we present detailed results on the complementary magnetic and thermomagnetic properties of the systems.

## Experimental

### Materials and methods

**Chemicals.** Iron(III)acetyl acetonate  $\text{Fe}(\text{acac})_3$  (99%) and 7-octenyltrimethoxysilane (OTS, 95%) are obtained from ABCR. Tetramethylammonium hydroxide ( $\text{NMe}_4\text{OH}$ , 25% in water) and poly(hydrogenmethylsiloxane) (PHMS,  $M_n = 1075 \text{ g mol}^{-1}$ ) are purchased from Sigma Aldrich. Potassium iodide KI (99%), 9-bromo-1-nonene (97%) and 4-cyano-4'-hydroxybiphenyl (99%) are bought from Alfa Aesar. Hexachloro-platin(IV)-acid hydrate  $\text{H}_2\text{Cl}_6\text{Pt}\cdot\text{H}_2\text{O}$  (Pt 37.3–38.0%) and 4-cyano-4'-pentybiphenyl (5CB, >98%) are purchased from TCI. Citric

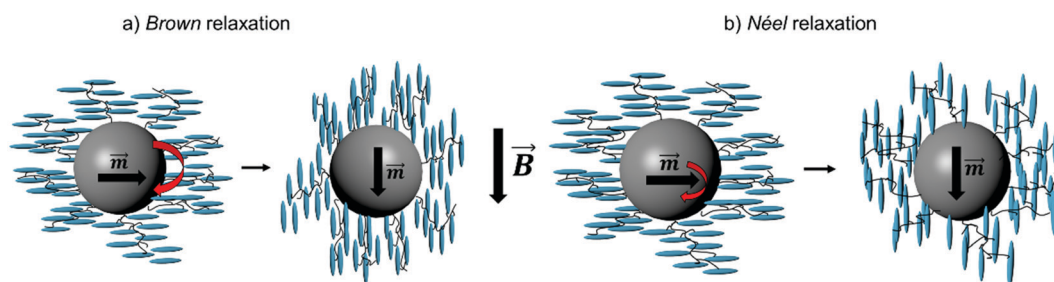


Fig. 1 Possible relaxation mechanism of nanoparticles in a magnetic field: Brown and Néel relaxation.



acid monohydrate ( $\geq 99.5\%$ ) is obtained from Jungbunzlauer GmbH. Acetone (99%), dichloromethane (DCM, HPLC), tetrahydrofuran (THF, HPLC grade), toluene (HPLC grade), magnesium sulfate  $\text{MgSO}_4$  (97%) are purchased from Acros Organics and potassium carbonate  $\text{K}_2\text{CO}_3$  ( $\geq 99\%$ ) is obtained from Fluka Analytical. Ethanol (HPLC), methanol (HPLC) and ethyl acetate (techn.) are purchased from Fisher Scientific. Deuterated chloroform ( $\text{CDCl}_3$ ) is obtained from Eurisotop.

### Synthetic procedures

**Synthesis of  $\text{Fe}_3\text{O}_4$  nanoparticles.**  $\text{Fe}_3\text{O}_4$  nanoparticles are obtained by thermal decomposition of  $\text{Fe}(\text{acac})_3$  in tri(ethylene glycol) and are electrostatically stabilized in water with citric acid using modified protocols from literature.<sup>45,46</sup> In brief, under argon atmosphere 7.2 mmol  $\text{Fe}(\text{acac})_3$  are dissolved in 100 ml tri(ethylene glycol), dehydrated at 180 °C for 1 h and heated to 280 °C for 2 h. After cooling down to room temperature the nanoparticles are precipitated by addition of 20 ml ethyl acetate on 5 ml of particle dispersion. The particles are collected by centrifugation, then redispersed again in 2 ml EtOH and the washing process is repeated for two times. Afterwards, the particles are washed two times with water and finally redispersed in 20 ml  $\text{H}_2\text{O}$ . Then, 2 ml of a 0.01 M solution of citric acid is added, treated with 30 s with ultrasonic bath, followed by addition of  $\text{NMe}_4\text{OH}$  solution till the pH is set to  $\sim 8$  to peptize the particles.

**Surface modification of  $\text{Fe}_3\text{O}_4$  with OTS.**  $\text{Fe}_3\text{O}_4$  nanoparticles are surface-functionalized with OTS using the procedure of Frickel *et al.*<sup>47</sup> The nanoparticles are added to ethanol/water mixture (30:1) at a concentration of 2 mg of NP per 1 ml of solution. Afterwards, OTS (3.6 mmol per 1 g of  $\text{Fe}_3\text{O}_4$ ) dissolved in ethanol is added dropwise over a period of 10 minutes, the reaction mixture is stirred at ambient temperature for 48 h. The  $\text{OTS}@Fe_3O_4$  are washed repeatedly with acetone by magnetic separation.

**Synthesis of mesogenic polymer 9OCB-PHMS.** The mesogenic polymer used in this work consists of 4-cyano-4'-nonenyloxybiphenyl (9OCB) as mesogenic unit and PHMS as polymeric precursor and is prepared using the procedure described in our previous work.<sup>21</sup> At first the mesogenic precursor 9OCB is synthesized by substitution of bromine from 9-bromo-1-nonene with 4-cyano-4'-hydroxybiphenyl with potassium carbonate and potassium iodide in acetone.

$^1\text{H-NMR}$  (499 MHz,  $\text{CDCl}_3$ ):  $\delta$  [ppm] = 7.76–7.59 (m, 4H), 7.53 (d, 2H), 6.99 (d, 2H), 5.82 (ddt, 1H), 5.10–4.89 (m, 2H), 4.01 (t, 2H), 2.18–1.96 (m, 2H), 1.94–1.71 (m, 2H), 1.53–1.44 (m, 8H).

Afterwards, the mesogenic polymer is prepared by platinum-catalyzed hydrosilylation reaction between PHMS and 4-cyano-4'-nonenyloxybiphenyl. The obtained polymer shows a functionalization degree of  $f_{9\text{OCB}} = 0.48$ .

$^1\text{H-NMR}$  (499 MHz,  $\text{CDCl}_3$ ):  $\delta$  [ppm] = 7.48 (d,  $J = 70$  MHz, 6H, aryl-H), 6.84 (s, 2H, aryl-H), 4.65 (s, 15H, Si-H), 3.85 (s, 2H, O- $\text{CH}_2$ ), 1.67 (s, 2H, alkyl-H), 1.22 (s, 14H, alkyl-H), 0.46 (s, 2H, Si- $\text{CH}_2$ ), 0.10–0.01 (m, 9H, Si- $\text{CH}_3$ ).

**Synthesis of polymer brush particles 9OCB-PHMS@ $\text{Fe}_3\text{O}_4$ .** The mesogenic polymer 9OCB-PHMS is coupled to  $\text{OTS}@Fe_3O_4$

in a platinum-catalyzed hydrosilylation reaction using our procedure.<sup>21</sup> Under nitrogen atmosphere,  $\text{OTS}@Fe_3O_4$  ( $n_{\text{OTS}} = 1$  eq.) dispersed in dry DCM are mixed with a moderate excess (1.5 eq.) of 9OCB-PHMS.  $\text{H}_2\text{Cl}_6\text{Pt}$  (0.002 eq.) in isopropanol is added to the reaction mixture, and the solution is heated to reflux for 72 h. The particles are collected by centrifugation and washed with dry DCM. In the last step, the particles are dispersed in dry THF.

**Preparation of ferronematic samples.** Magnetically doped LC dispersions are prepared by mixing 5CB and a respective amount of  $9\text{OCB-PHMS}@Fe_3O_4$  dispersed in THF in a glass vial. The solvent is removed by placing the dispersion in the vacuum drying oven at 70 °C for 24 h. The magnetic volume ratio is determined by VSM measurements. The obtained stock solution is diluted with 5CB in order to obtain a concentration series. After adding 5CB, the dispersions are treated in the ultrasonic bath at 40 °C for 10 minutes and quenched in cold water.

### Methods

**Transmission electron microscopy (TEM).** TEM images are taken using a Zeiss LEO 912 Omega. The instrument is equipped with a 120 kV  $\text{LaB}_6$  cathode and a Moorweis Slow Scan with a CCD camera Sharp:Eye 2048  $\times$  2048 TR. The sample is drop-casted to a copper-coated carbon grid and left for slow evaporation.

**Nuclear magnetic resonance spectroscopy ( $^1\text{H-NMR}$ ).** NMR spectra are measured on a Bruker Advance III 499 spectrometer ( $^1\text{H-NMR}$ : 499.2 MHz) with  $\text{CDCl}_3$  as solvent.

**Vibrating sample magnetometry (VSM).** VSM experiments of powder samples and samples in dispersions are performed on an ADE Magnetics EV7 vibrating sample magnetometer equipped with a GMW electromagnet 3472-70 with a maximum field strength of  $2.8 \times 10^8$  A  $\text{m}^{-1}$  under sample vibration frequency of 75 Hz. The obtained magnetization curve is corrected by subtraction of the diamagnetic part. From the initial slope of the magnetization curve in solvent the magnetic susceptibility  $\chi_{\text{ini}}$  can be derived, and the magnetic moment  $m$  can be calculated according to eqn (1)

$$m = \frac{3k_{\text{B}}T\chi_{\text{ini}}}{M_{\text{s}}\mu_0} \quad (1)$$

with  $\mu_0$  as magnetic constant and  $M_{\text{s}}$  as the saturation magnetization. With the magnetic moment, the magnetic diameter  $d_{\text{m}}$  of the particles is obtained with eqn (2).

$$d_{\text{m}} = \sqrt[3]{\frac{6m}{M_{\text{s}}\pi}} \quad (2)$$

**SQUID magnetometer (SQUID).** Superconducting Quantum Interference Device (SQUID) magnetometry is used to perform temperature- and field-dependent magnetic characterization of the LC based samples by using a Quantum Design MPMS-5S SQUID magnetometer. The zero-field cooled (ZFC) and field-cooled (FC) magnetization curves are recorded in a temperature range of 5–350 K with a sweeping rate of 2 K per minute and



with an applied magnetic field of 10 mT, unless otherwise stated. For the ZFC–FC protocol, the sample is cooled down from room temperature to 5 K at zero field, then the small magnetic field is applied and the ZFC magnetization is measured continuously while heating the sample from 5–350 K. The FC magnetization is recorded, while the sample is cooled subsequently from 350 K to 5 K within the small magnetic field of 10 mT.

**Infrared (IR) spectroscopy.** IR spectra are taken on a Shimadzu IR Affinity-1 FT-IR spectrometer using total reflectance technique (ATR). The measurement range is 4500–600 cm<sup>-1</sup>.

**Differential scanning calorimetry (DSC).** DSC measurements are performed on a METTLER Toledo DSC 821e calorimeter with a nitrogen cooling system. The thermal behavior of a sample between –50 °C to 50 °C is investigated by heating with a heating rate of 2 K m<sup>-1</sup> and cooling with a cooling rate of 5 K m<sup>-1</sup>.

**Refractive index measurements.** Refractive index measurements are performed on a Krüss AR4 Abbé refractometer for the determination of the order parameter  $S$ , that describes the orientational order of a liquid crystalline system.  $S$  is a measure for the average deviation of the mesogens from the overall nematic director orientation and is defined by eqn (3).

$$S = \frac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle \quad (3)$$

with  $\theta$  the angle between the nematic director and the long axis of the individual molecules.<sup>48</sup> The temperature dependence of the order parameter follows the Haller approximation<sup>49,50</sup>

$$S = \left( 1 - \frac{T}{T_{\text{NI}}} \right)^\beta \quad (4)$$

with  $\beta$  being the critical exponent and  $T_{\text{NI}}$  being the temperature for the nematic–isotropic transition temperature. The order parameter can be calculated from refractometry measurements using Vuks relationship<sup>51</sup>

$$S \left( \frac{\Delta\alpha}{\alpha} \right) = \frac{3(n_e^2 - n_o^2)}{n_e^2 + 2n_o^2 - 3} \quad (5)$$

with  $\Delta\alpha$  anisotropy of polarizability and  $\alpha$  mean molecular polarizability.

For this method, of the ordinary and the extraordinary refractive indices  $n_o$  and  $n_e$  are measured as a function of temperature and  $S$  is determined by plotting  $\ln \left( \frac{3(n_e^2 - n_o^2)}{n_e^2 + 2n_o^2 - 3} \right)$  versus  $\ln \left( 1 - \frac{T}{T_{\text{NI}}} \right)$ . Using the fact that  $S = 1$  for a virtually fully ordered nematic system, the intercept at  $T = 0$  of the resulting linear plot gives the result for  $\ln \left( \frac{\Delta\alpha}{\alpha} \right)$ , allowing the calculation of  $S$  from eqn (5) for every temperature, respectively. The slope of the linear plot gives the value for the critical exponent  $\beta$ .

**Dielectric measurements.** Dielectric measurements in electric and magnetic fields are performed using a Solatron 1260A impedance analyser in commercial glass cells (EHC, Japan)

equipped with planar transparent indium tin oxide (ITO) electrodes (thickness: 25 μm, resistance: 10 Ω) and a parallelly rubbed polyimide layer for LC planar alignment. The Fréedericksz transition is studied using the capacitance measurement technique at 5 kHz of the driving voltage.

#### Simulation of electric and magnetic Fréedericksz transition.

In general, the electric and magnetic thresholds  $U_0$  and  $H_0$  of this transition in a pure nematic in splay geometry are related to the system's splay elastic constant  $K_1$ , and its dielectric or magnetic anisotropy as given by eqn (6) and (7), respectively.

$$U_0 = \pi \sqrt{\frac{K_1}{\epsilon_0 \Delta\epsilon}} \quad (6)$$

$$H_0 = \frac{\pi}{D} \sqrt{\frac{K_1}{\mu_0 \Delta\chi}} \quad (7)$$

with  $\Delta\epsilon$  and  $\Delta\chi$  being the dielectric and diamagnetic susceptibility anisotropy of the nematic mesogen and  $D$  the thickness of the cell. The corresponding characteristic properties such as the electric threshold  $U_0$  and the splay constant  $K_1$  are obtained based on the exact analytical equations for the director field in the cells. In case of the electric Fréedericksz transition, the voltage drop across the cell  $U$  is related to the tilt of the director  $\theta(z)$  with respect to the cell normal and the threshold voltage  $U_0$  by the following integral expression:

$$\frac{U}{U_0} = \frac{2}{\pi} \int_{\xi_0}^{\pi/2} \left( \frac{(1 + \gamma \sin^2 \theta_m)(1 + p \sin^2 \theta_m \sin^2 \xi)}{(1 + \gamma \sin^2 \theta_m \sin^2 \xi)(1 - \sin^2 \theta_m \sin^2 \xi)} \right)^{1/2} d\xi \quad (8)$$

In the magnetic case, the relation is described by:

$$\frac{\pi H}{2 H_c} = \int_{\xi_0}^{\pi/2} \left( \frac{1 + p \sin^2 \theta_m \sin^2 \xi}{1 - \sin^2 \theta_m \sin^2 \xi} \right)^{1/2} d\xi \quad (9)$$

with the elastic anisotropy parameter  $p = \frac{K_3 - K_1}{K_1}$ , the dielectric

anisotropy  $\gamma = \frac{\Delta\epsilon}{\epsilon_\perp}$ , the perpendicular component of the dielectric

permittivity  $\epsilon_\perp$ ,  $\Delta\epsilon = \epsilon_\parallel - \epsilon_\perp$ ,  $\xi_0 = \arcsin \left( \frac{\sin \theta_0}{\sin \theta_m} \right)$ , the pretilt angle

$\theta_0$  between the nematic director and the substrate, the director deflection angle in the midplane of the cell  $\theta_m$ , and

$H_c = \frac{H_0}{\pi} = D^{-1} \sqrt{K_1 / \mu_0 \Delta\chi}$ . The equation for the effective dielectric permittivity is

$$\epsilon_{\text{eff}} = d \left( \int_0^d \frac{1}{\epsilon_\perp + \Delta\epsilon \sin^2 \theta(z)} dz \right)^{-1} \quad (10)$$

Eqn (8)–(10) define the effective dielectric constant  $\epsilon_{\text{eff}}$  as a function of the voltage  $U$  or magnetic field strength  $H$ .

For ferromagnetic systems, an additional cross-coupling condition is introduced by assuming an effective interaction between the magnetic director of the doping particles, and the director of the nematic phase. Our approach is an adaption of the model developed by Podoliak *et al.*,<sup>52</sup> based on the continuum theory developed by Buylov and Raikher<sup>10</sup> and





discussed for  $\text{CoFe}_2\text{O}_4$  in our previous work<sup>21</sup> is qualitatively confirmed by ATR-IR spectroscopy (see ESI,† Fig. S1a) by comparing the spectra of the 9OCB-PHMS and carefully washed 9OCB-PHMS@NP after the attachment procedure. More quantitative information on the functionalization is obtained by TGA from the mass loss of carefully dried powders before and after polymer functionalization (Fig. S1b, ESI†). With the mass loss, a specific particle functionality of  $f_{9\text{OCB},\text{p}} = 1.32 \text{ mmol g}^{-1}$  is estimated. Taking into account the particle sizes obtained from TEM and a core density of  $\rho = 5.2 \text{ g cm}^{-3}$ ,<sup>53</sup> the surface functionalization density  $\sigma_A$  can be determined to be nearly 13 molecules of 9OCB per  $\text{nm}^2$ . For the fabrication of stable ferronematic phases, 9OCB-PHMS@ $\text{Fe}_3\text{O}_4$  dispersed in THF are added to pure 5CB. After evaporation of the solvent, the particles are dispersed by ultrasonication in the isotropic phase at  $T = 40 \text{ }^\circ\text{C}$ . By quenching the dispersion in a water bath at room temperature, a stable colloidal ferronematic stock dispersion is obtained.

### Magnetic properties of core particles and ferronematic samples

The magnetic properties of the carefully dried core particles and the core particles dispersed in water and 5CB are investigated by vibrating sample magnetometry (VSM). The normalized magnetization curves from powder-based experiments and aqueous solution compared to a magnetization curve of particles dispersed in 5CB are shown in Fig. 4.

The core particles possess a saturation magnetization of  $M_s = 61.2 \text{ A m}^2 \text{ kg}^{-1}$  which is close to the  $M_s$  of  $\text{CoFe}_2\text{O}_4$  particles used in our previous work ( $M_s = 71.4 \text{ A m}^2 \text{ kg}^{-1}$ ).<sup>21</sup> With the magnetic susceptibility  $\chi_{\text{ini}}$  which is derived from the magnetization curves of the particles dispersed in water, the magnetic moment and the magnetic diameter are determined to be  $m = 1.17 \times 10^{-19} \text{ A m}^2$  and  $d_m = 8.5 \text{ nm}$ . Compared to the aqueous solution, the magnetization curve of 9OCB-PHMS@ $\text{Fe}_3\text{O}_4$  particles in 5CB shows no significant differences. For dried  $\text{Fe}_3\text{O}_4$  nanoparticles no hysteresis but superparamagnetic behaviour can be observed which is in agreement with the results of other works.<sup>54</sup>

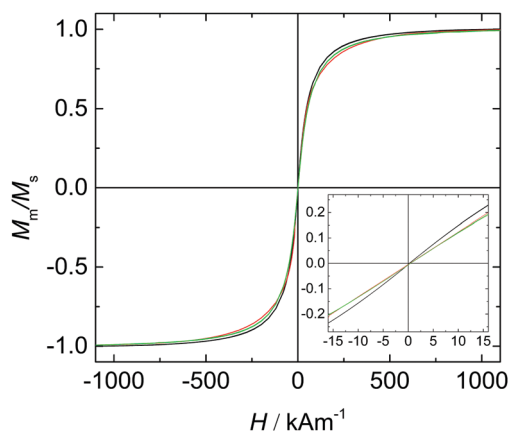


Fig. 4 Magnetization curves of a dried  $\text{CA@Fe}_3\text{O}_4$  particles (—),  $\text{CA@Fe}_3\text{O}_4$  particles dispersed in water (—) and 9OCB-PHMS@ $\text{Fe}_3\text{O}_4$  particles in 5CB (—).

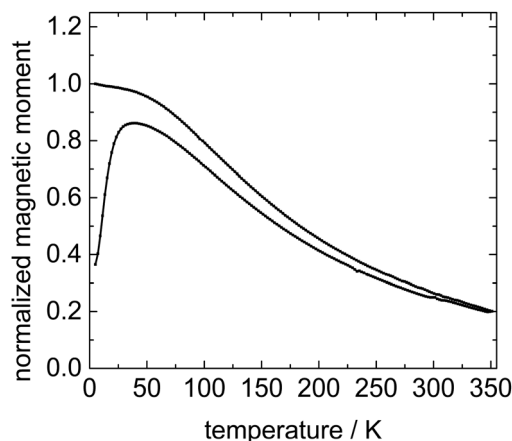


Fig. 5 Normalized ZFC-FC magnetization curves recorded at 10 mT for 9OCB-PHMS@ $\text{Fe}_3\text{O}_4$  in 5CB.

In order to get information about the magnetic relaxation behaviour of the particles in the host matrix 5CB, the ferronematic samples are investigated by temperature-dependent superconducting quantum interference device (SQUID) magnetometry using an applied field of 10 mT. The ZFC-FC magnetization curves of 9OCB-PHMS@ $\text{Fe}_3\text{O}_4$  particles in 5CB are depicted exemplarily for a concentration of  $\phi_m = 4.7 \times 10^{-4}$  in Fig. 5.

The zero-field cooled magnetization increases first and then decreases after reaching a maximum at around 45 K which corresponds to the blocking temperature  $T_B$ . Below this temperature the particles are mainly blocked in terms of Néel relaxation. Moreover, both ZFC and FC curves nearly coincide at high temperatures. Thus,  $\text{Fe}_3\text{O}_4$  particles in 5CB predominately are superparamagnetic and relax according to the Néel mechanism which is described with the Néel time  $\tau_N$  constant:<sup>55</sup>

$$\tau_N = \tau_{N,0} \exp\left(\frac{K_{\text{eff}} V_{\text{core}}}{k_B T}\right) \quad (16)$$

with  $\tau_0$  as the time constant for the relaxation, typically assumed to be of a magnitude of  $\tau_0 = 10^{-9} \text{ s}$ ,  $K_{\text{eff}}$  being the effective anisotropic constant,  $k_B$  as the Boltzmann constant,  $T$  as the temperature and  $V_{\text{core}}$  as the volume of the particle.

With the blocking temperature  $T_B$  of  $\text{Fe}_3\text{O}_4$  and the effective anisotropy constant  $K_{\text{eff}} = 13 \text{ kJ m}^{-3}$ ,<sup>54</sup> the mean volume of the particles is approximately calculated according eqn (17)

$$V = \frac{25k_B T_B}{K_{\text{eff}}} \quad (17)$$

with the obtained volume of  $V = 1.24 \times 10^{-24} \text{ m}^3$  a mean particle diameter of  $d = 12.3 \text{ nm}$  is estimated which is in good accordance with mean diameter of the particles determined by TEM images.

### Thermal properties of ferronematic samples

The impact of 9OCB-PHMS@ $\text{Fe}_3\text{O}_4$  on the stability of 5CB in dependence on the concentration is investigated with differential scanning calorimetry (DSC). From the two endothermic peaks of



the thermograms (see ESI,† Fig. S2) the crystalline to the nematic phase transition temperature  $T_{\text{CN}}$  and the nematic to the isotropic phase transition temperature  $T_{\text{NI}}$  are extracted. In Fig. 6a and b, the difference of the transition temperatures  $\Delta T_{\text{CN}}$  and  $\Delta T_{\text{NI}}$  to 5CB are plotted as a function of the solid doping volume fraction  $\phi_s$ , respectively.

The values for both  $T_{\text{CN}}$  and  $T_{\text{NI}}$  increase at small doping fractions and decrease again above a magnetic volume fraction of  $\phi_s = 1.8 \times 10^{-4}$ . In general, the values for the transition temperatures for 5CB doped with 9OCB-PHMS@Fe<sub>3</sub>O<sub>4</sub> are slightly higher. The existence of stable nematic phases for all doping fractions proves a good compatibility between LC phase and nanoparticles as already shown for 9OCB-PHMS@CoFe<sub>2</sub>O<sub>4</sub> and 9OCB-PHMS@SiO<sub>2</sub> particles.

### Influence of 9OCB-PHMS@NP on order parameter

The order parameters of 5CB doped with the superparamagnetic 9OCB-PHMS@Fe<sub>3</sub>O<sub>4</sub> particles at different solid doping fractions are examined by measuring the refractive indices as a function of temperature and employment of the Haller method. The values for the order parameter as a function of the solid volume fraction  $\phi_s$  are shown in Fig. 7a. With increasing particle concentration, the order parameter increases. The positive impact on the order parameter of the system further denotes an improved compatibility between nanoparticles and liquid crystalline phase. In Fig. 7b, the critical exponents  $\beta$  for 5CB doped with 9OCB-PHMS@Fe<sub>3</sub>O<sub>4</sub> and with 9OCB-PHMS@CoFe<sub>2</sub>O<sub>4</sub> extracted from the Haller plot are depicted as function of the solid volume ratio  $\phi_s$ . In general,  $\beta$  is a parameter for the description of the behaviour of  $S$  near the phase transition. For pure 5CB, a critical exponent of  $\beta = 0.17$  is found which is consistent with the value found in literature for this method.<sup>56</sup> The nematic–isotropic transition is known to be weakly first-order.<sup>57,58</sup> With increasing  $\phi_s$  the critical exponent  $\beta$  first decreases steeply and then approaches a constant value. This phenomenon can be assigned to the weakly-first order transition becoming more continuous and thus, more akin to second order.

### Capacitance measurement of ferronematics

The impact of 9OCB-PHMS@Fe<sub>3</sub>O<sub>4</sub> nanoparticles on the electro and magneto–nematic response is investigated by dielectric spectroscopy measurements in planar aligned sandwich cells as it was done for 9OCB-PHMS@CoFe<sub>2</sub>O<sub>4</sub>. The electric transition for 5CB doped with 9OCB-PHMS@Fe<sub>3</sub>O<sub>4</sub> with different magnetic volume ratios are displayed in Fig. 8.

In general, the dielectric permittivity as a function of electric field strength exhibits the expected shape. At fields below a critical field amplitude  $U_0$  (threshold) the permittivity remains constant with the value of  $\epsilon_{\perp}$ . After exceeding the threshold strength, the permittivity increases as the mesogens align in the direction of the electric field. With increasing doping fraction, all curves weakly deviate from the behavior of pure 5CB.

To get more quantitative information, the electric transition data are fitted using eqn (8) and (10) with the elastic constants  $K_1$  and  $K_3$ , the parallel component of the dielectric permittivity,  $\epsilon_{\parallel}$ , and the pretilt angle  $\theta_0$  between the nematic director and the substrate as fitting parameters.<sup>48</sup> The fitting results for the system doped with Fe<sub>3</sub>O<sub>4</sub> are presented in Table 1. The values for  $U_0$  and  $K_1$  remain nearly constant, with a slight increase for the highest magnetic volume fractions which can be an indication for the presence of particle–particle interaction.

Finally, the magneto–nematic response of the ferronematics is analysed to investigate the effect of superparamagnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticles on the LC phase 5CB. Therefore, the LC sandwich cells are placed in a static magnetic field applied perpendicular to the cell plane and the dielectric permittivity is measured as a function of the magnetic field. The magnetic Fréedericksz transition of 5CB and 5CB doped with 9OCB-PHMS@Fe<sub>3</sub>O<sub>4</sub> in different volume ratios are displayed in Fig. 9a. In the present arrangement, pure 5CB, which is well-explored in literature,<sup>59–63</sup> exhibits a transition at  $H_0 = 200 \text{ kA m}^{-1}$ . By doping 5CB with 9OCB-PHMS@Fe<sub>3</sub>O<sub>4</sub> the course of the magnetic transition changes drastically with increasing doping fraction. Even at very low concentration of  $\phi_m = 1.9 \times 10^{-5}$  the graphs do not show the

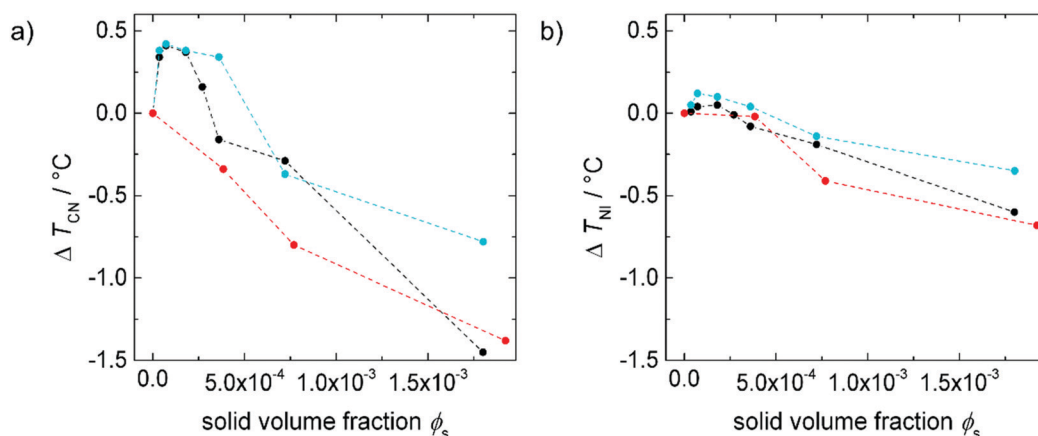


Fig. 6 Difference of (a) crystal–nematic transition temperature  $\Delta T_{\text{CN}}$  and (b) nematic–isotropic transition temperature  $\Delta T_{\text{NI}}$  of doped 5CB to pure 5CB as a function of magnetic dopant particle volume fraction  $\phi_s$  with 9OCB-PHMS@Fe<sub>3</sub>O<sub>4</sub> (●), 9OCB-PHMS@CoFe<sub>2</sub>O<sub>4</sub> (●) and 9OCB-PHMS@SiO<sub>2</sub> (●) as doping agents. The values for 9OCB-PHMS@CoFe<sub>2</sub>O<sub>4</sub> and 9OCB-SiO<sub>2</sub> are taken from ref. 21.



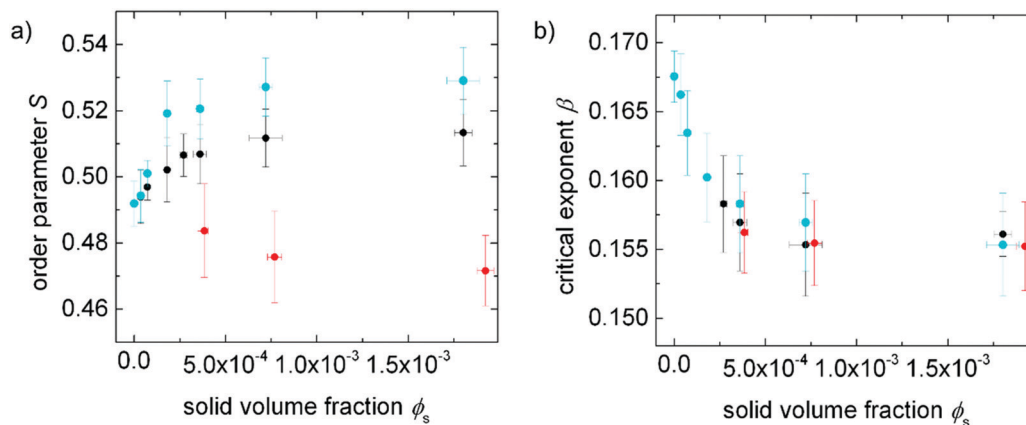


Fig. 7 (a) Order parameter at a reduced temperature of  $\tau = 0.985$  and (b) critical exponent  $\beta$  as a function of solid volume fraction  $\phi_s$  for 5CB doped with 9OCB-PHMS@Fe<sub>3</sub>O<sub>4</sub> (●), 9OCB-PHMS@CoFe<sub>2</sub>O<sub>4</sub> (●), and 9OCB-PHMS@SiO<sub>2</sub> (●). The values for 9OCB-PHMS@CoFe<sub>2</sub>O<sub>4</sub> and 9OCB-PHMS@SiO<sub>2</sub> are taken from ref. 21.

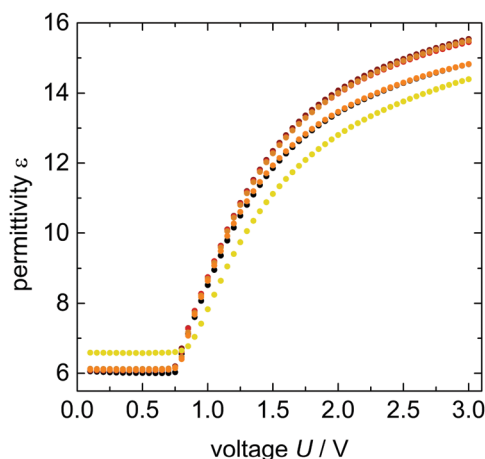


Fig. 8 Permittivity  $\epsilon$  as a function of electric field for 5CB (●) and 9OCB-PHMS@Fe<sub>3</sub>O<sub>4</sub> doped 5CB with different magnetic volume fraction  $\phi_m = 1.9 \times 10^{-5}$  (●),  $\phi_m = 9.4 \times 10^{-5}$  (●),  $\phi_m = 1.9 \times 10^{-4}$  (●),  $\phi_m = 4.7 \times 10^{-4}$  (●) and  $\phi_m = 9.4 \times 10^{-4}$  (●).

Table 1 Obtained values for  $U_0$ ,  $\epsilon_{\parallel}$ ,  $\theta_0$ ,  $K_1$  and  $K_3$  determined from electric Fréederickzs transition for 9OCB-PHMS@CoFe<sub>2</sub>O<sub>4</sub> in various magnetic volume fractions

$\phi$	$U_0/V$	$\epsilon_{\parallel}$	$\theta_0$	$K_1/pN$	$K_3/pN$
0	0.79	17.59	$3.8 \times 10^{-3}$	6.70	7.78
$1.9 \times 10^{-5}$	0.74	18.37	$3.8 \times 10^{-3}$	6.05	7.64
$9.4 \times 10^{-5}$	0.75	18.26	$3.8 \times 10^{-3}$	6.05	7.34
$1.9 \times 10^{-4}$	0.75	18.37	$3.8 \times 10^{-3}$	6.21	7.40
$4.7 \times 10^{-4}$	0.77	17.46	$3.8 \times 10^{-3}$	5.78	6.27
$9.4 \times 10^{-4}$	0.84	17.53	$7.2 \times 10^{-3}$	6.77	9.45

sharp transition typically observed for 5CB. Above a concentration of  $\phi_m = 9.4 \times 10^{-5}$  the curves additionally feature a shoulder at low magnetic fields. At a magnetic volume fraction of  $\phi_m = 5 \times 10^{-4}$  a threshold field of only  $\sim 15 \text{ kA m}^{-1}$  or 18 mT is observed. Taking into account the values of  $\epsilon_{\perp}$  which remain

nearly constant, the change in the magnetic transition is not caused by weakening of the anchoring at the glass/LC interface but attributed to a strong magneto-nematic coupling. The volume ratio of mesogens oriented in the direction of the magnetic field  $\nu_{\text{NF}}$  approximately is obtained using the measured permittivity at a given magnetic field  $\epsilon_B$ , the initial and final permittivity  $\epsilon_{\perp}$  and  $\epsilon_{\parallel}$  and by using eqn (18)

$$\nu_{\text{NF}} = \frac{\epsilon_B - \epsilon_{\perp}}{\epsilon_{\parallel} - \epsilon_{\perp}} \quad (18)$$

Fig. 9b plays the ratio  $\nu_{\text{NF}}$  as a function of magnetic volume ratio  $\phi_m$  for different magnetic fields below the magnetic threshold for pure 5CB. With increasing doping fraction  $\phi_m$  the ratio of oriented mesogens increases nearly linearly (Fig. 9c).

In order to get more information about the magnitudes of the coupling, the experimental data for the ferromagnetic systems doped with Fe<sub>3</sub>O<sub>4</sub> are analogously fitted with the model based on Burylov and Raikher<sup>10</sup> with  $\Delta\chi$  and  $K_1$  as obtained from the electrical transition simulation, and  $\kappa$  and  $\omega$  as the fitting parameters. The fitted simulations are given as black lines in Fig. 9a while the obtained fitting parameters  $\omega$  as a function of the fitting parameter  $\kappa$  is displayed in Fig. 9c.

In general, satisfactory fits are obtained for the present experiments. As expected,  $\kappa$  and  $\omega$  increase approximately linearly with increasing volume fraction  $\phi_m$ . With the quotient  $\omega/\kappa$  from the slope of  $\omega$  versus  $\kappa$  being 0.45 we can calculate the effective coupling energy density per particle using eqn (14) to be  $\Omega = 1.17 \times 10^4 \text{ N m}^{-2}$ . By taking the particle size into account according to eqn (15), the surface anchoring strength is determined to be  $W_s = 1.47 \times 10^{-4} \text{ J m}^{-2}$ .

### Comparison of Fe<sub>3</sub>O<sub>4</sub> and CoFe<sub>2</sub>O<sub>4</sub>

In this work, the effect of superparamagnetic Fe<sub>3</sub>O<sub>4</sub> particles on 5CB is investigated in order to compare it with the behaviour of magnetically blocked particles. As for superparamagnetic particles, the mechanical reorientation of the particles in response to the application of a magnetic field is prevented due to magnetic reorientation, further information about the



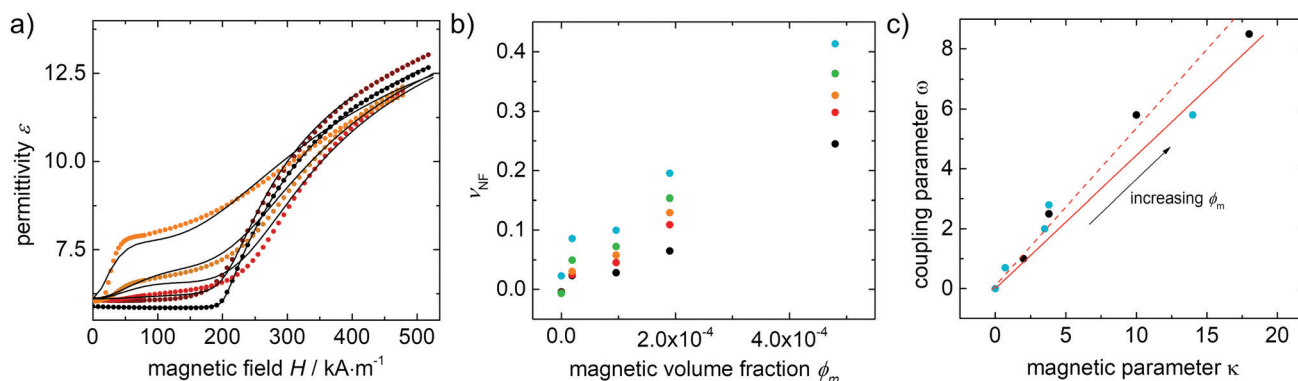


Fig. 9 (a) Magnetic Freederiksz transition. Dielectric permittivity as a function of magnetic field for 5CB and 9OCB-PHMS@Fe<sub>3</sub>O<sub>4</sub> doped 5CB in different magnetic volume fractions  $\phi_m = 1.9 \times 10^{-5}$  (●),  $\phi_m = 9.4 \times 10^{-5}$  (●),  $\phi_m = 1.9 \times 10^{-4}$  (●) and  $\phi_m = 4.7 \times 10^{-4}$  (●). (b) Ratio of mesogens oriented in field direction  $\nu_{\text{NF}}$  as a function of magnetic volume ratio  $\phi_m$  at different magnetic field strengths of  $H = 40 \text{ kA m}^{-1}$  (●),  $H = 80 \text{ kA m}^{-1}$  (●),  $H = 120 \text{ kA m}^{-1}$  (●),  $H = 160 \text{ kA m}^{-1}$  (●),  $H = 200 \text{ kA m}^{-1}$  (●). (c) Dimensionless parameters  $\omega$  versus  $\kappa$  describing the magnetic coupling of the director and the magnetisation for 5CB doped with 9OCB-PHMS@Fe<sub>3</sub>O<sub>4</sub> (●) with the corresponding linear regression (—) compared to 5CB doped with 9OCB-PHMS@CoFe<sub>2</sub>O<sub>4</sub> (●) and its corresponding linear regression (---).

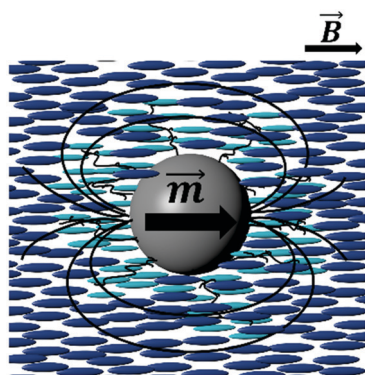


Fig. 10 Schematic illustration of a LC polymer-decorated magnetic nanoparticle in a LC host matrix and an applied external field. The covalently bond polymer brush is partly swollen with host mesogens.

origin of the coupling in such a ferronematic system can be obtained with this approach. For a better compatibilization with 5CB, the particles are modified with LC polymer brushes using our successful approach.<sup>21</sup>

Detailed information about the surface functionalization and magnetic properties of the employed particles are listed in the ESI† (Tables S1 and S2). The synthesized Fe<sub>3</sub>O<sub>4</sub> particles exhibit a comparable size, particle brush, saturation magnetization and magnetic moment to the CoFe<sub>2</sub>O<sub>4</sub> particles used in our previous works. The magnetization curves further reveal a hysteresis and remanence for CoFe<sub>2</sub>O<sub>4</sub> indicating a considerable magnetically blocked state at ambient temperature, while for Fe<sub>3</sub>O<sub>4</sub> no hysteresis is observed. For more information about the magnetic properties, ZFC/FC measurements are performed. Here, for Fe<sub>3</sub>O<sub>4</sub> the superparamagnetic state is confirmed with a blocking temperature of 45 K, but no definite jumps due to the change in mobility of particles because of the melting and crystallization 5CB is observed. In contrast, the ZFC curves of CoFe<sub>2</sub>O<sub>4</sub> particles in 5CB (Fig. S3, ESI†) do not show a maximum

and do not coincide with the FC curve as the blocking temperature is not reached within the temperature range of the measurement confirming the magnetically blocked state. Moreover, a characteristic jump in the FC curve can be observed at 308 K which can be attributed to the transition from the isotropic to the nematic phase.

The measurement of thermal properties using DSC proves for both particle types a good stability of the nematic phase. As already observed for 9OCB-PHMS@CoFe<sub>2</sub>O<sub>4</sub>, by doping 5CB with 9OCB-PHMS@Fe<sub>3</sub>O<sub>4</sub> the order parameter is increased with increasing doping concentration with slightly higher values for Fe<sub>3</sub>O<sub>4</sub> which can be assigned to a good compatibility between nanoparticles and liquid crystalline phase. In contrast, non-magnetic 9OCB-PHMS@SiO<sub>2</sub> particles decrease the order of the system. By performing electric capacitance measurements, the elastic constants  $K_1$  and  $K_3$  are obtained which remain nearly constant with increasing doping fraction.

Information about the magneto–nematic coupling is obtained by magnetic capacitance measurements. For ferronematic phases doped with 9OCB-PHMS@CoFe<sub>2</sub>O<sub>4</sub>, as well as doped with 9OCB-PHMS@Fe<sub>3</sub>O<sub>4</sub>, the threshold drastically decreases with respect to particle fraction. In both systems, a measurable magnetic response is obtained at field strengths of  $\sim 15 \text{ kA m}^{-1}$  or 18 mT at magnetic volume fractions of  $\phi_m = 5 \times 10^{-4}$ . Quantitative information about the coupling in the ferronematic systems are determined by an appropriate fitting procedure. Partly unexpected by our initial hypothesis, the magnetic capacitance results of both particle types are qualitatively and quantitatively quite similar (see Table 2), indicating that an analogous effect on the nematic host phase can be achieved as well by doping with magnetically blocked or superparamagnetic particles that are covered with a liquid crystalline polymer brush. This observation indicates that in contrast to our initial hypothesis, a permanent magnetic moment of the dopant particles is not a prerequisite for the observed phenomenon. A major difference in the response to an external magnetic field is that a blocked particle undergoes a



mechanical rotation to remagnetize while this is not a requirement for superparamagnetic particles. Accordingly, the mechanical rotation of the particles is not of critical influence for the phenomenon. Instead, we propose the following qualitative mechanistic explanation by individually addressing the different coupling modes present in the systems. Therefore, we approximate roughly the distance dependent magnetic field strength caused by a single dipolar particle of magnetic moment  $m$ .

By approximating the particle as a point dipole with a stationary direction and strength, the magnetic flux  $B$  of the dipole as a function of the distance to the point dipole  $r_d$  can be calculated according to eqn (19).

$$B(r_d) = \frac{\mu_0 m}{2\pi r_d^3}. \quad (19)$$

For the magnetic Fréedericksz transition in pure 5CB, typically a critical magnetic flux of about 100–200 mT is required, depending on the thickness of the employed cell. If we consider this value as a measure for the required field strength for interaction, it seems plausible that the mesogens in the environment of the particle are affected by the orientation of its magnetic moment up to a distance of about 5–10 nm. Within this distance, we find the mesogenic units that are covalently attached to the polymer brush shell (Fig. 10).

It is verified by work of others that the creation of such a shell drastically changes the situation of interaction.<sup>22,43</sup> Without the surface functionalization, the LC host molecules couple directly with the surface of the nanoparticles. As a result, doping with NP leads to the distortion of the nematic phase that is compensated with the formation of defects.<sup>9,25</sup> Further it was shown that covalently bound polymer chains on planar surfaces can be manipulated by an external trigger due to the balance of the stretching of the chains and their flexibility.<sup>64–66</sup> This phenomenon can be transferred to spherical surfaces, that are functionalized with LC polymer brushes. With this approach, a buffer zone between the host molecules and the particle is established that can minimize the formation of defects. This leads to a high density of mesogens in the area where the magnetic field lines from the magnetic moment of the particle is dense which further facilitates the alignment. This way, the development of a dipolar defect caused by the particle, as usually reported for spherical particles, might be prevented as already indicated by similar observations.<sup>43</sup> We can further propose that the shell is swollen with 5CB molecules from the host liquid crystal to a considerable extend

and that also those mesogens are affected by the field (see Table 1). Such a magnetic alignment layer within the host in the particle vicinity is supported also by the observations on the particle influence on the nematic–isotropic transition temperature and on the order parameter that both indicate a stabilizing impact of the dopants on the nematic phase even in the absence of a magnetic field.

While this seems plausible at least for the magnetically blocked particles, our observations made for the superparamagnetic particles only on the first glance contradict the explanation. In the case of superparamagnetic particles, no significant magnetic field is expected in time average. However, in a small external field even for short relaxation times, the particles exhibit on average a preferred orientation along the field axis, which further increases with field strength. Thus, for superparamagnetic particles with a similar magnetic moment  $m$  a shell orientation can be expected induced by an external field. This orientation further influences the alignment of the whole matrix by interaction of the polymer-attached mesogens with the adjacent host mesogens. In order to give a precise explanation for the coupling theoretical calculations or more experiments are necessary.

## Conclusions

We successfully implemented our concept for the compatibilization of  $\text{CoFe}_2\text{O}_4$  to  $\text{Fe}_3\text{O}_4$  nanoparticles with nematic liquid crystalline phases to fabricate stable ferronematic materials based on particles with different magnetic relaxation behaviour. The composite materials are based on particles with covalently bound mesogenic polymer and 5CB as LC host.

9OCB-PHMS@ $\text{Fe}_3\text{O}_4$  particles are synthesized by thermal composition of  $\text{Fe}(\text{acac})_3$  and subsequent surface functionalization with a liquid crystalline brush. They show similar values for the size, surface functionalization density and magnetic moment compared to 9OCB-PHMS@ $\text{CoFe}_2\text{O}_4$ . However,  $\text{CoFe}_2\text{O}_4$  are magnetically blocked and  $\text{Fe}_3\text{O}_4$  particles are superparamagnetic.

The strong compatibilization of 9OCB-PHMS@ $\text{Fe}_3\text{O}_4$  in 5CB is proven by DSC. As for  $\text{CoFe}_2\text{O}_4$ , stable nematic phases with high volume fractions of up to  $\phi_m = 9.6 \times 10^{-4}$  can be prepared. Moreover, the addition of modified  $\text{Fe}_3\text{O}_4$  to 5CB also leads to an increase of the order parameter.

By magneto-optical measurements in planarly aligned cells we could clearly show a considerable influence on the magnetic Fréedericksz transition as already observed for  $\text{CoFe}_2\text{O}_4$  as doping agent. The system is sensitive to magnetic fields of the order of tens of milli tesla even for low concentration of  $\phi_m = 4.7 \times 10^{-4}$ . A quantitative analysis and thus, calculation of the effective coupling energy density per particle  $\Omega$  and the surface anchoring strength  $W_s$  is performed with obtained values comparable to  $\text{CoFe}_2\text{O}_4$ . As for superparamagnetic  $\text{Fe}_3\text{O}_4$  particles the orientational coupling due to a mechanical anchoring of the mesogens and the particle surface is excluded, the magneto-optic effects can be induced by a direct coupling

**Table 2** Slope  $\omega/\kappa$ , coupling energy density per particle  $\Omega$  and surface anchoring strength  $W_s$  for 5CB doped with 9OCB-PHMS@ $\text{CoFe}_2\text{O}_4$  and 9OCB-PHMS@ $\text{Fe}_3\text{O}_4$

Doping agent	$\omega/\kappa$	$\Omega/\text{N m}^{-2}$	$W_s/\text{J m}^{-2}$
9OCB-PHMS@ $\text{Fe}_3\text{O}_4$	0.79	17.59	$3.8 \times 10^{-3}$
9OCB-PHMS@ $\text{CoFe}_2\text{O}_4^a$	0.74	18.37	$3.8 \times 10^{-3}$

<sup>a</sup> Taken from ref. 21.



over the stray field or the formation of aggregates. Both effects are strengthened by the covalently bound LC polymer brush at the particle surface. However, the origin of this coupling is not fully understood yet.

In general, these hybrid systems are promising material for magnetically driven devices and gaining a deeper insight of the coupling promotes the technical realization and optimization of such devices.

## Conflicts of interest

There are no conflicts to declare.

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