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Experimental assessment of interactions between liquid crystal 4-cyano-4′-hexylbiphenyl and magnetoferritin

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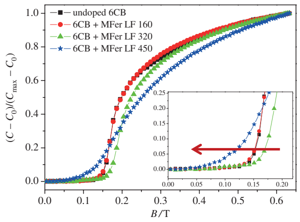
The response of 4-cyano-4′-hexylbiphenyl (6CB) liquid crystal to external magnetic field increased upon the addition of biocompatible magnetoferritin nanoparticles. Physico-chemical properties of magnetoferritin were characterized by UV/VIS spectrophotometry and dynamic light scattering, zeta potential, and superconducting quantum interference device magnetometry measurements. The interaction between 6CB liquid crystal and magnetoferritin was examined by capacitance measurements.

Reduced capacitance *vs.* magnetic field in a low magnetic field region



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The study of anisotropic liquid crystals (LCs) possessing a combination of the properties of liquids (isotropic liquid phase, fluidity) and crystalline solids (orientation arranging of molecules), which have found use in display technology, is of interest to condensed matter physics.[1,2] The basic criteria for finding and synthesizing LCs suitable for commercial use in imaging displays were their high chemical stability, reduced transition temperature (to room temperature), and reduced melting point. An important property of LCs is their response to external electric field associated with their reorientation exhibiting the so-called Fréedericksz transition.[3] LCs can be applied as thermovision cameras in electro-optical devices used in medicine.[4] However, they are less sensitive to magnetic fields due to their very low anisotropy of diamagnetic susceptibility ($\chi_a \approx 10^{-7}$). Therefore, attention has been focused on increasing the sensitivity of LCs to external magnetic field for creating magnetically tunable structures with spontaneous polarization and dielectric permittivity enhancement based on preparing a complex system containing magnetic nanoparticles (ferronematics) for new technologies. In this context, the LCs can be used for the construction of LC displays,[5] photonics,[6] magneto-optics,[7] nanosensing and biosensing[8] devices and LC sensors for magnetic field detection (magnetovision cameras).[9] Nematic LCs doped with ferroelectric nanoparticles improve dielectric and optical anisotropy, electro-optical response,[10,11] and photorefractive properties of composites.[12] The nanoparticle–LC composites are metamaterials that provide very high or low and negative refractive index, permittivity, and/or permeability values,[13] which are important properties for photonic materials.

We focused on a well-characterized thermotropic nematic LC, 4-cyano-4′-hexylbiphenyl (6CB), with high chemical stability and a convenient temperature range of the liquid crystal phase.[14] The 6CB LC was successfully doped with magnetic nanoparticles of different sizes and shapes.[9,15] For biomedical engineering, new biocompatible iron oxide-based nanomaterials are required, for example, magnetoferritin (MFer) consisting of a spherical protein shell of apoferritin with an external size of around 10–12 nm, which surrounds max. ~8 nm-sized polyphase core of magnetic iron oxide/(oxo)hydroxide nanoparticles (magnetite, maghemite, and/or lepidocrocite-like nanocrystals).[16–19] The physico-chemical properties of MFer were investigated,[16,20–23] interesting effects were discovered,[20,24] and different bioapplications were explored.[16,25] Nevertheless, the synthesis technology of MFer should be improved to obtain higher colloidal stability of MFer nanoparticles in aqueous solution and to increase the magnetic susceptibility of the nanoparticles for potential biomedical applications.[16,25]

Here, we consider the sensitivity of 6CB LC doped with MFer nanoparticles at different loading factors (LFs), *i.e.* the average numbers of iron atoms per apoferritin biomacromolecule, to applied electric and magnetic fields. The colloidal stability, magnetic properties, and structural transitions were studied by magnetization, dynamic light scattering, zeta potential and capacitance measurements.

At the first step, we prepared aqueous colloidal solutions of MFer with LFs of 160, 320 and 450. The amount of iron and theoretical values of LFs were set to below 600[20] prior to synthesis in order to ensure colloidal stability without large aggregates of MFer with 6CB.

The average hydrodynamic diameters of magnetoferritin obtained by dynamic light scattering measurements $<D_{\mathrm{HYDR}}>$ were 18.05, 20.76 and 44.31 nm at LF of 160, 320 and 450, respectively. The increase of the size of hydrated/solvated protein macromolecules can be related to the partial destruction or agglomeration of a small fraction of proteins upon iron loading caused by protein–protein interaction or by the magnetic character of MFer nanoparticles observed previously.[20]

The ζ-potentials of MFer nanoparticles in colloidal solutions at comparable concentrations, dissolved in an AMPSO buffer

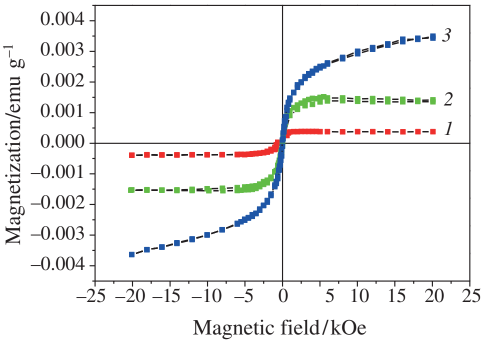

Figure 1 Magnetization–field dependences of MFer with LFs of (*1*) 160, (*2*) 320, and (*3*) 450.

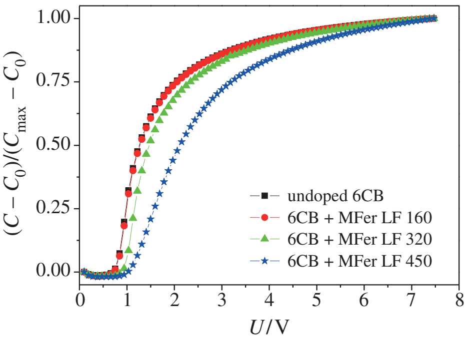

Figure 3 Dependence of the reduced capacitance of the LC 6CB and the FNs on the applied voltage U in the classical electric Fréedericksz transition.

with pH 8.6, were –26.3, –26.7 and –26.6 mV for MFer with LF 160, 320 and 450, respectively. These measurements confirmed a negative surface charge of proteins and good colloidal stability.

Magnetization measurements revealed a superparamagnetic behaviour of MFer nanoparticles without X-ray powder diffraction analysis, which in the previous work[16] confirmed lepidocrocite-like nanocrystals, where however the presence of other phases (magnetite/maghemite nanocrystals) was not excluded. We suggested various iron core compositions of MFer samples. Magnetization–field curves for MFer powder samples (Figure 1) normalized to the total sample mass indicated an increase in magnetization with LF, which is a typical magnetization–LF relationship.[25] Contributions from the protein coat, apoferritin, and sample capsule were subtracted.

The LC 6CB was doped with MFer powders suspended in a solvent with continuous stirring (LFs of 160, 320 and 450) to have the same volume concentration ($\varphi = 10^{-2}$) (Figure 2). These samples demonstrated that the FNs with LF of 450 had the lowest stability, and NP aggregates were formed at the bottom of a container. Therefore, colloidal stability depends on the LF in MFer. Despite the fact that magnetoferritin exhibited good colloidal stability according to zeta potential measurements, the mixture of interacting LC and MFer powder samples may have different physico-chemical properties including colloidal stability, which decreased with raising LF (Figure 2).

Zeta potential measurements showed very low colloidal stability of the mixtures: 0.0286, 0.0387 and 0.0396 mV at LF 160, 320 and 450, respectively. The interaction of 6CB with MFer biomacromolecules changed the total negative surface charge of MFer on which 6CB was adsorbed. Based on the observed behavior, we propose the MFer surface modification with chelates or surfactants for various LC anchoring to improve adsorption and growth of the colloidal stability. By analogy with traditional LCs, the biological ones like lipid membranes are good candidates for biomedical applications since they act as biocompatible molecules with an amphiphilic structure that protect inorganic nanoparticle surface coating important for delivering drugs.[26–28]

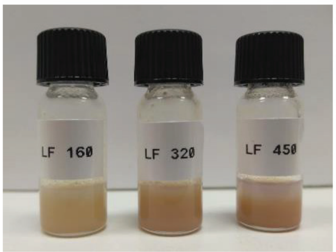

Figure 2 Ferronematics with MFer at LFs of 160, 320, and 450.

Figure 3 shows the voltage dependence of the reduced capacitance (see Online Supplementary Materials) of the FNs demonstrating that the electric Fréedericksz transition threshold is shifted towards higher voltages with increasing MFer LF.

Figure 4 represents the reduced capacitance *vs*. the external magnetic induction B dependence in the undoped 6CB and FNs based on MFer with different LFs. In case of the lowest LF 160, the critical magnetic field H_C does not shift very significantly. Doping of LC with higher LF 320 caused an increase in H_C as the presence of MFer to impeded LC molecules in their reverse orientation to the direction of the applied magnetic field. However, a further increase in LF up to 450 led to a smearing of magnetic Freedericksz transition. It can be explained by the presence of aggregates in this sample (Figure 2) caused by the larger size of MFer. Previously, we studied the role of a surfactant layer in the LC composite and observed similar phenomena.[29] With increasing particle size, the thickness of the stabilisation layer on NPs decreased and the magnetic attraction between particles rose. However, at LF of 450 in MFer, the FN was more sensitive to the applied magnetic field in a low-field region (see Figure 4) even much below the classical magnetic Fréedericksz threshold.

Thus, we studied the influence of the LF of MFer in 6CB-based FNs on a shift of the critical magnetic field. The addition of the MFer affected the sensitivity of FNs to external magnetic fields due to bounding between MFer and LC molecules. Experimental results indicated that doping of MFer with LF 160

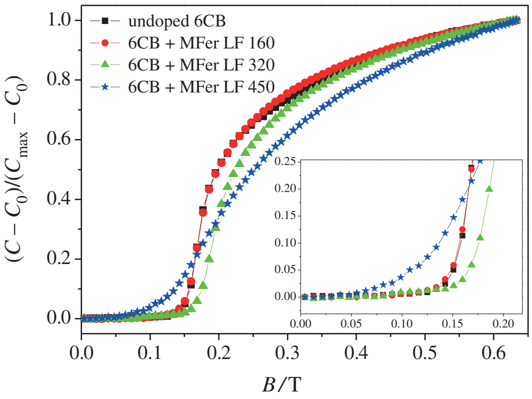

Figure 4 Reduced capacitance *vs*. the external magnetic field for undoped and doped 6CB with MFer in different LFs measured at $U = 0.1$ V. Inset: reduced capacitance *vs*. magnetic field in the low magnetic field region.

shifted the critical field of the magnetic Fréedericksz transition to almost negligible one and for LF 320 the critical threshold was much more pronounced. In the case of LF 450, smearing of structural transition was observed. So we can conclude that different LFs of MFer are important in tuning the sensitivity of such bio-hybrid systems. However, the increment of LFs results in low colloidal stability, which should be improved for a future potential applications.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.01.024.

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