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# Exceptionally large magneto-optical response in dispersions of plate-like nanocrystallites and magnetic nanoparticles

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## ABSTRACT

We introduce a binary colloidal system with an exceptionally strong magneto-optical response. Its induced optical birefringence at even low magnetic fields (in the mT range) reaches a value with the same order of magnitude as that of nematic liquid crystals. This system is based on a binary mixture of plate-like, non-magnetic pigment nanoparticles and a small volume fraction ( <1v%) of spherical magnetic nanoparticles. In the field-free state, the suspension is isotropic. Birefringence is caused by an alignment of the pigment platelets, commanded by shape-anisotropic agglomerates of the magnetic nanoparticles in an external magnetic field. We give a semiquantitative discussion about this.

Colloidal suspensions of anisometric (shape-anisotropic) particles exhibit a variety of unique properties, depending on particle concentrations and on external electric fields. Among those are the formation of ordered phases, reversible phase separations, electro-optical switching, and non-linear rheology. Electro- and magneto-optical properties are of particular interest because of potential applications in electrophoretic ink displays, magneto-optical switches and other technologies. There has been a long history of attempts to combine optical properties of molecular liquid crystals (LC) with magnetic properties of ferrofluids by doping nematic phases, following an idea of Brochard and de Gennes [1]. For a long time, these were only partially successful (e.g. [2–4]): The nature of the nematic mesophase often leads to a segregation of the magnetic dopants and degradation of the samples, stability of the suspensions is the main problem. Polymer and elastomer LC doped with ferroparticles are an alternative [5]. Recently, it was shown that suspensions of nano-platelets in nematic liquid crystals can even produce weakly ferromagnetic fluids [6–12].

Here, we use a different strategy and replace the molecular mesogens by suspensions of shape-anisotropic crystals in a non-polar solvent. Lyotropic LC phases formed by dispersed shape-anisotropic particles have been extensively studied in various colloidal systems such as goethite suspensions, fd- and tobacco-mosaic viruses, or clays [13–17]. The existence of ordered phases above critical particle concentrations was predicted by Onsager in the late forties [18]. Inks of elongated pigment needles (Novoperm Carmine) exhibit such a nematic phase already at concentrations as low as 12 v%, and even at lower concentrations, in the isotropic state, these suspensions show an enhanced optical response to external electric fields [19,20]. These pure pigment suspensions do not show appreciable magnetically-induced birefringence in weak (mT) fields. The diamagnetic needles align perpendicular to an external magnetic field at very high field strengths (15–20 T).

In order to achieve an appreciable magneto-optical response at mT fields, one can dope such suspensions with magnetic nanoparticles (MNP). Suspensions of magnetic $Fe_3O_4$ particles with shape-anisotropic $V_2O_5$ crystals were shown to exhibit a command effect that can be exploited in magneto-optic switching by Slyusarenko and Kredentser et al. [21,22]. They demonstrated that the orientation of the dispersed magnetic nanorods is transferred by sterical interactions to the non-magnetic component of the mixture. They also described this effect using an Onsager-type theory of binary mixtures [23]. This effect was investigated quantitatively in dispersions of magnetically doped suspensions of $V_2O_5$ needles [22], where the magnetically induced birefringence reached $1.2 \cdot 10^{-4}$.

In the present study, we dope platelet-like non-magnetic nanocrystals with MNP. Even though the individual MNP are spherical, they form anisometric aggregates in magnetic fields, that are able to command the alignment of the much larger crystallites [24]. We will demonstrate here that this effect is even more

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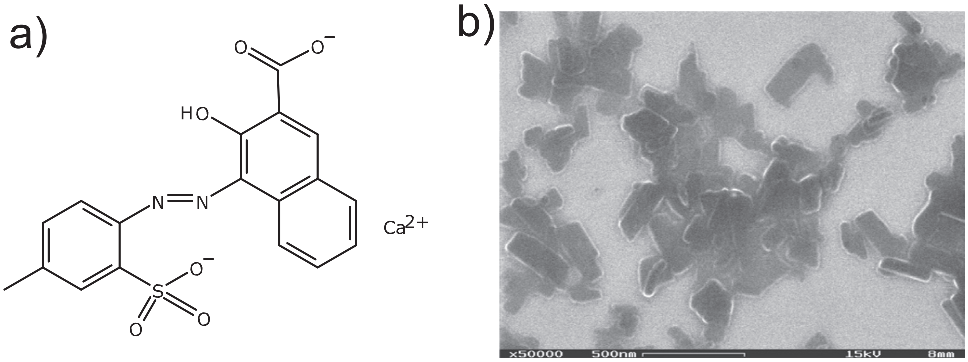

**Fig. 1.** (a) Chemical formula of a C.I. Pigment Red 176, (b) Scanning electron microscopy (SEM) image of the pigment particles Permanent Rubine, image size 2.3 μm × 1.7 μm.

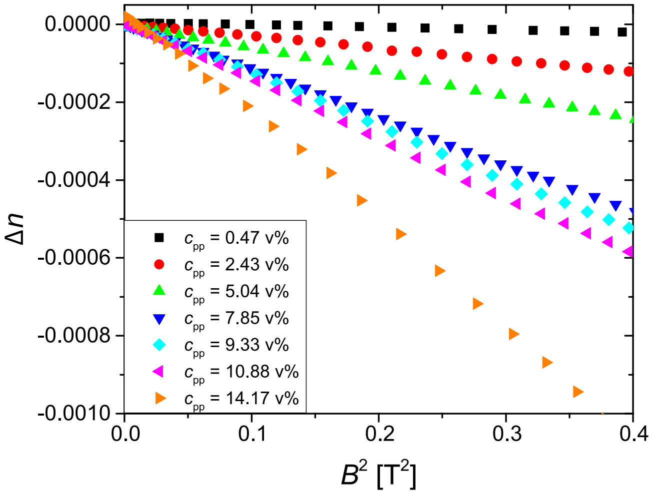

**Fig. 2.** Magnetically induced birefringence in dispersions of Permanent Rubine in dodecane at various volume fractions.

pronounced for diamagnetic platelet-shaped pigment particles, where the orientation of the platelets in the magnetic field changes with the presence of magnetic particles. The induced optical anisotropy exceeds the Cotton–Mouton-effect of conventional materials by orders of magnitude.

The material used here is Pigment Red 57:1 in its commercially available form *Permanent Rubine L4B01* (*Clariant*, Frankfurt/M, used as received). It is a yellow shade Calcium laked BONS Red pigment. The molecular structure formula of the pigment is shown in Fig. 1a. The primary particles are platelets with an average length of 180 nm ± 81 nm, average width of 64 nm ± 22 nm and an average thickness of 12 nm ± 8 nm [25] (Fig. 1b).

Pigment particles were suspended in the nonpolar solvent dodecane (*Sigma-Aldrich*, Hamburg, used as received) with a commercially available dispersant Solsperse 11200 (*Lubrizol*, Brussels, used as received). Initially, suspensions with pigment concentrations of 20 wt% and above were prepared by milling with the addition of the stabilizer (150 wt% of Solsperse per weight of the pigment). The mixture was milled in a planetary mill (Fritsch Pulverisette 7 premium line), using 0.3 mm yttria stabilized zirconia beads in zirconia lined pots (total 60 min at 500 rpm). Appropriate cooling cycles prevented the temperature inside the pots from rising above 60 °C. Concentrations below 20 wt% were made by stepwise dilution of the base suspension. To test the stability of the suspensions, samples were centrifuged at 10,000 rpm for 60 min. None of the concentrations showed any phase separation into particle-rich and particle-poor zones. Samples left untouched for 12 months did not show any phase separation or aggregation. The suspensions were doped with a commercially available ferrofluid (*Ferrotec*, APG 935). This ferrofluid contains spherical magnetite particles with the diameter of about 10 nm, suspended in hydrocarbons. The surfactant layer thickness is estimated to be about 2 nm. In order to get homogenous mixtures, 3 cycles of about 3 min each in an ultrasonic bath were performed. Dilution for different concentrations of particles was done with dodecane.

Birefringence was measured in sandwich ITO cells (*E.H.C.* and *Instec*) of thicknesses 10 μm or 5 μm. We used the Voigt geometry in which the light direction is perpendicular to the magnetic field, and the polariser and analyzer is oriented at ±45° (to the field direction), respectively. In this geometry, we employed a well-established photoelastic modulator technique [26–28] to measure the optical anisotropy (birefringence $\Delta n$). The modulator introduces a time-dependent optical phase shift $\phi(t) = A\sin(\omega t)$. The transmitted light intensity was recorded using a photodetector with the signal measured by a lock-in amplifier. Two Fourier amplitudes of the time dependent photodetector signal are recorded, $V_\omega$ and $V_{2\omega}$. The value of the birefringence is given by

$$\Delta n = \frac{\lambda}{2\pi d}\arctan\left(\frac{V_\omega}{V_{2\omega}}\frac{J_2(A)}{J_1(A)}\right),$$

where $\lambda = 632.8$ nm is the laser wavelength and $d$ is the cell thickness. $J_n(A)$ are the Bessel functions of the first kind of integer order $n$.

Pure dispersions of the Permanent Rubin show a negative birefringence in a magnetic field [29]. This is shown in Fig. 2. The pigment particles behave diamagnetically and appear to have a negative magnetic anisotropy.

The Cotton–Mouton constant calculated from linear fits of the field dependent birefringence is shown in Fig. 3.

The ferrofluid diluted with dodecane also shows very low field-induced birefringence (see Fig. 4). Since the MNP particles are spherically shaped, the birefringence can be attributed to the

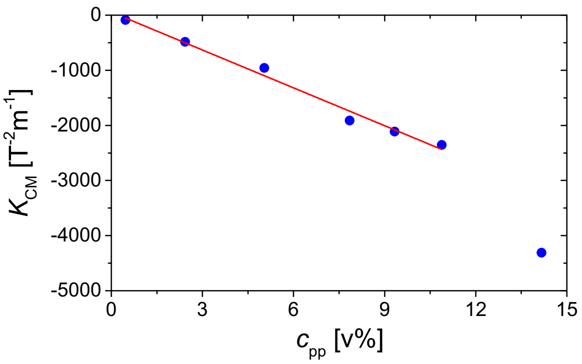

**Fig. 3.** Cotton–Mouton constant of Permanent Rubine in dodecane at various volume fractions.