Enhanced magnetic-field-induced optical properties of nanostructured magnetic fluids by doping nematic liquid crystals

Xiang Wang, Shengli Pu*, Hongzhu Ji and Guojun Yu

Abstract
Ferronematic materials composed of 4-cyano-4′-pentylbiphenyl nematic liquid crystal and oil-based Fe₃O₄ magnetic fluid were prepared using ultrasonic agitation. The birefringence (Δn) and figure of merit of optical properties (Q = Δn/α, where α is the extinction coefficient) of pure magnetic fluids and the as-prepared ferronematic materials were examined and compared. The figure of merit of optical properties weighs the birefringence and extinction of the materials and is more appropriate to evaluate their optical properties. Similar magnetic-field- and magnetic-particle-concentration-dependent properties of birefringence and figure of merit of optical properties were obtained for the pure magnetic fluids and the ferronematic materials. For the ferronematic materials, the values of Q increase with the volume fractions of nematic liquid crystal under certain fixed field strength and are larger than those of their corresponding pure magnetic fluids at high field region. In addition, the enhancement of Q value increases monotonously with the magnetic field and becomes remarkable when the applied magnetic field is beyond 50 mT. The maximum relative enhanced value of Q exceeds 6.8% in our experiments. The results of this work may conduce to extend the pragmatic applications of nanostructured magnetic fluids in optical field.

Keywords: Magnetic fluids, Nematic liquid crystals, Ferronematic materials, Birefringence, Figure of merit of optical properties

Background
Magnetic fluid (MF) is a kind of stable colloidal suspension of small magnetic particles with typical sizes of 10 nm. The liquid carrier may be either an aqueous or a non-polar solvent. The nanoparticles are coated with a surfactant layer, such as oleic acid and polymer, which will prevent agglomeration by overcoming the van der Waals attractive forces between the particles. The Brownian motion can keep the nanoparticles from settling under gravity [1]. MF was firstly invented in the mid-1960s, and then the study and applications of MF have been extended to multidisciplinary sciences, such as chemistry, fluid mechanics, and magnetics. Recently, with the fast development of MF, it has been broadly used for dynamic sealing, shock absorbers, audio loudspeaker coolant, and biomedical sciences [2,3]. Because of the dramatic development of optical communication and integrated optics, the optical properties of MF have attracted a great deal of attention from researchers since the late part of the twentieth century, which include tunable refractive index [4], birefringence [5], Faraday effect [6], optical transmittance [7,8], optical scattering [9,10], and so on. Most of these are based on the fluid behavior and magnetism of the MF. Until now, several potential applications of MF to optical devices have been proposed, such as MF optical switches [11], MF gratings [12], MF light modulation [13], MF optical fiber modulator [14], and MF optical limiting [15]. Recently, some experimental investigations about the magneto-optical effects of binary, multiple-phase, ionic, and doped MFs show that these kinds of MFs can present some unique optical properties [16–19].

Nematic liquid crystal has attracted a great deal of attention from researchers owing to its optical birefringence and scattering properties, which can be controlled by the external stimuli, such as electrical, magnetic fields, and shear stresses [20]. Usually, a strong magnetic field is needed to study the magnetic-field-induced...
optical properties of liquid crystals. This is due to the small anisotropic diamagnetic susceptibility ($\Delta \gamma$) of the liquid crystal [21]. To lower the applied magnetic field, liquid crystal doped with ferromagnetic grains (the corresponding mixture is denoted as ferronematic material) has been proposed [21,22]. Burylov and Raikher have reported that magneto-optical response of a liquid crystalline system can be enhanced by uniformly doping with ferromagnetic grains and the orientational state of the ferronematic material can be fully controlled by a rather weak magnetic field (much less than 10 mT) [23]. Raikher and Stepnov have discussed a transient birefringence response of a nematic liquid crystal doped with single-domain ferromagnetic particles and have derived a set of coupled macroscopic equations describing the evolution of the director texture and the magnetization distribution within the ferronematic material during the change of the external field [24]. It has been disclosed that many properties of liquid crystal can be improved and enhanced by doping with ferromagnetic grains, which are favorable for practical applications [25–28]. Considering the unique properties of MFs and ferronematic materials, doping MFs with nematic liquid crystal is attractive and needs further in-depth investigation. To the best of our knowledge, few experiments about the attractive and needs further in-depth investigation. To the best of our knowledge, few experiments about the magnetic-field-induced birefringence of the as-prepared mixture is denoted as ferronematic material) has been proposed [21,22]. Burylov and Raikher have reported that magneto-optical response of a liquid crystalline system can be enhanced by uniformly doping with ferromagnetic grains and the orientational state of the ferronematic material can be fully controlled by a rather weak magnetic field (much less than 10 mT) [23]. Raikher and Stepnov have discussed a transient birefringence response of a nematic liquid crystal doped with single-domain ferromagnetic particles and have derived a set of coupled macroscopic equations describing the evolution of the director texture and the magnetization distribution within the ferronematic material during the change of the external field [24]. It has been disclosed that many properties of liquid crystal can be improved and enhanced by doping with ferromagnetic grains, which are favorable for practical applications [25–28]. Considering the unique properties of MFs and ferronematic materials, doping MFs with nematic liquid crystal is attractive and needs further in-depth investigation. To the best of our knowledge, few experiments about the magnetic-field-induced birefringence of the as-prepared mixture is denoted as ferronematic material) has been proposed [21,22]. Burylov and Raikher have reported that magneto-optical response of a liquid crystalline system can be enhanced by uniformly doping with ferromagnetic grains and the orientational state of the ferronematic material can be fully controlled by a rather weak magnetic field (much less than 10 mT) [23]. Raikher and Stepnov have discussed a transient birefringence response of a nematic liquid crystal doped with single-domain ferromagnetic particles and have derived a set of coupled macroscopic equations describing the evolution of the director texture and the magnetization distribution within the ferronematic material during the change of the external field [24]. It has been disclosed that many properties of liquid crystal can be improved and enhanced by doping with ferromagnetic grains, which are favorable for practical applications [25–28].

### Methods

#### Preparation of ferronematic materials

The ferronematic materials investigated in this work are a mixture of MFs and nematic liquid crystals. The oil-based Fe3O4 MF with volume fraction of 5.62% was provided by Ferrotec Corporation (Chuo-ku, Tokyo, Japan). The 4′-cyanopentylbiphenyl (C18H19N) nematic liquid crystal (5CB) was provided by Shijiazhuang Huarui Scientific and Technological Co., Ltd (Shijiazhuang, Hebei, China). The MF was diluted with the liquid paraffin carrier (provide by Sinopharm Chemical Reagent Co., Ltd, Shanghai, China) with ultrasonic agitation of about 2 h. The as-prepared pure MF samples have four different concentrations of magnetic particles, referred as samples a (1:8), b (1:10), c (1:12), and d (1:14). The numbers in the brackets indicate the volume ratio of MF to liquid paraffin used to mix. The volume fractions of the magnetic particle for samples a, b, c, and d are 0.62%, 0.51%, 0.43%, and 0.37%, respectively, as shown in Table 1.

| Sample | Volume ratio of MF to liquid paraffin | Volume fraction of magnetic particle |
|--------|--------------------------------------|-------------------------------------|
| a      | 1:8                                  | 0.62%                               |
| b      | 1:10                                 | 0.51%                               |
| c      | 1:12                                 | 0.43%                               |
| d      | 1:14                                 | 0.37%                               |

To investigate the optical properties of ferronematic materials with different concentrations of magnetic particles, 1 ml of 5CB and 3 ml of any one of sample a, b, c, or d are mixed to obtain samples a-5CB, b-5CB, c-5CB, and d-5CB, respectively. The volume fractions of 5CB of these samples are the same (25.00%). Their magnetic particle volume fractions are 0.47%, 0.38%, 0.34% and 0.28%, respectively, as shown in Table 2.

Similarly, a series of samples with a constant concentration of magnetic particle and different concentrations of 5CB are prepared and shown in Table 3. They are denoted as samples MF-5CB, MF-5CB(2), MF-5CB(3), and MF-5CB(4). The volume fraction of magnetic particle is fixed at 0.50%. Their volume fractions of 5CB are 23.08%, 19.34%, 15.24%, and 10.72%, respectively.

#### Experiments

The magnetic-field-induced birefringence of the as-prepared ferronematic samples can be measured by the light extinction method, which consists of a sample cell placed between accurately set ‘crossed’ polarizers as shown in Figure 1 [29]. A single-mode He-Ne laser emitting linearly polarized light with a wavelength of 632.8 nm is employed. The propagation direction of the incident light is normal to the applied magnetic field. The thin film sample is placed between a pair of solenoids, which generate a uniform horizontal magnetic field in the sample region. The strength of magnetic field can be adjusted by tuning the magnitude of the supply current. For the birefringence measurement, the optimum angle of the polarization direction of the incident linearly polarized light with respect to the magnetic field should be around π/4 [30]. At a given magnetic field,
the light transmittance after the analyzer is investigated. Through rotating the analyzer, the maximum and minimum transmitted intensities ($I_{\text{max}}$ and $I_{\text{min}}$) are measured, respectively. The birefringence $\Delta n$ can be determined according to the following:

$$\Delta n = \arcsin \left( \frac{2 \sqrt{I_{\text{min}}/I_{\text{max}}} \sqrt{h_1 - h_2}}{1 + I_{\text{min}}/I_{\text{max}}} \right) \lambda / (2nd),$$

where $d$ equals 170 $\mu$m and $\lambda$ is 632.8 nm; $h_i (i = 1, 2)$ are the electric field absorption coefficients for the polarization direction of the incident light parallel and being perpendicular to the magnetic field, respectively, which can be obtained by solving $I_i = I_0 e^{-2h_i(h)} I_{oi}$ and $I_i$ are the transmitted intensities of the sample under zero and certain magnetic field. Therefore, the birefringence of the sample as a function of magnetic field can be acquired by measuring $I_{\text{max}}$, $I_{\text{min}}$, $I_{oi}$, and $I_i$ at different magnetic fields.

### Results and discussion

Figure 2 shows the birefringence of pure MFs with different magnetic particle concentrations as a function of magnetic induction. From Figure 2, we can see that the birefringence of samples a to d increases gradually with the magnetic induction and tends to saturate at high field. This is attributed to the formation of magnetic chains under external magnetic field. Application of external magnetic field will induce structural ordering within the MF confined between two glass plates, which are due to the interaction between the magnetic dipoles induced at the particle sites [31,32]. This results in the optical anisotropy of MF under applied magnetic field. When the applied magnetic field is small, the aligned discrete magnetic short chains will form. With further increasing the strength of the magnetic field, the short chains will start to combine with each other to become longer discrete chains. The longer the chain structure is, the stronger the spatial anisotropy is and the larger the birefringence of MF becomes.

Figure 2 also indicates that samples with high volume fraction of magnetic particle have high birefringence under the same field strength. Low concentration of magnetic particles will lead to weak interaction between magnetic particles under the fixed field. The average distance between the magnetic particles within the samples will then become relatively large. Therefore, the number of chains per unit area will decrease as the concentration

### Table 3 Concentrations of samples MF-5CB, MF-5CB(2), MF-5CB(3), and MF-5CB(4)

| Sample   | Volume fraction of magnetic particle | Volume fraction of 5CB |
|----------|--------------------------------------|------------------------|
| MF-5CB   | 0.50%                                | 23.08%                 |
| MF-5CB(2)| 0.50%                                | 19.34%                 |
| MF-5CB(3)| 0.50%                                | 15.24%                 |
| MF-5CB(4)| 0.50%                                | 10.72%                 |

Figure 1 Schematic of the experimental setup for measuring the birefringence of the ferronematic materials.

Figure 2 Birefringence of pure MFs and MFs doped with 5CB. Birefringence of pure MFs with different magnetic particle concentrations and MFs doped with 5CB as a function of magnetic induction.
of magnetic particles decreases, which contributes to the low degree of structure anisotropy and then small value of birefringence of the sample under low field.

The experimental results for the corresponding ferro- nematic samples (samples a-5CB, b-5CB, c-5CB, and d-5CB) are also shown in Figure 2, which are very similar to those of the pure MF samples. Table 2 shows that all the ferro- nematic samples have the same volume fraction of 5CB (25.00%) but have different magnetic particle volume fractions, so the variation in birefringence between different ferro- nematic samples is attributed to the change of magnetic particle concentration. Besides, the birefringence of the ferro- nematic samples is weaker than those of the corresponding pure MF samples. This is probably assigned to the decrease of magnetic particle concentration through doping 5CB.

To further investigate the influence of 5CB concentration on the birefringence of ferro- nematic samples, the birefringence of samples MF-5CB, MF-5CB(2), MF-5CB (3), and MF-5CB(4) is also measured, and the experimental results are shown in Figure 3. Table 3 shows that all the ferro- nematic samples have the same volume fraction of magnetic particles (0.50%) but have different 5CB volume fractions. The $\Delta n$-$B$ curves for different samples in Figure 3 almost overlap with each other, which mean that only the magnetic particle concentration is crucial to the birefringence of the samples, and 5CB concentration has no influence on the birefringence of the samples.

For most practical applications to MF-based photonic devices, the values of birefringence and transmittance of the materials are two very critical parameters. Pure MFs and ferro- nematic materials with higher magnetic particle concentration have higher absorption, though they have a higher value of birefringence. The figure of merit of optical properties $Q$ defined as $\Delta n/\alpha$ may be appropriate to evaluate their optical properties. The larger the value of $Q$ is, the better the optical properties of the samples are. Though 5CB does not contribute to the birefringence, it will lessen the extinction coefficient of the sample, which will be beneficial to enhance the value of $Q$. To obtain the value of $Q$, the extinction coefficient $\alpha$ of the first two series of samples (Tables 1 and 2) as a
function of magnetic induction are measured and shown in Figure 4. Figure 4 indicates that the extinction coefficient does not change with the field strength for a given sample. Moreover, the sample with higher volume fraction of magnetic particle has a larger extinction coefficient.

The calculated value of $Q$ of the pure MFs and their corresponding ferronematic samples as a function of magnetic induction is plotted in Figure 5. From Figure 5, we can see that the value of $Q$ for samples a to d increases gradually with the applied magnetic field and tends to saturate at high field, while the value of $Q$ does not vary with the magnetic particle concentration under the same field strength. This means that the magnetic particle concentration has no influence on the figure of merit of optical properties of the samples. The magnetic-field-dependent values of $Q$ for the corresponding ferro-nematic samples (samples a-5CB, b-5CB, c-5CB, and d-5CB) are very similar to those of the pure MF samples. However, the ferronematic samples have larger values of $Q$ than their corresponding pure MF samples at high field region. When doped with 5CB, the magnetic particle concentration of the ferronematic samples will reduce compared with the corresponding pure MF samples. This
will result in the decrease of birefringence and the increase of transparency of the sample. The experimental results in Figure 5 indicate that the latter effect outweighs the former one at high field region. This leads to the augment of the value of $Q$, i.e., enhanced optical properties for the ferro nematic materials at high field region. Figure 5 also implies that 5CB is crucial to the figure of merit of optical properties of the samples and that magnetic particle concentration has no influence on the figure of merit of optical properties of the samples.

To quantify the enhanced optical properties, the relative enhancement of the $Q$ value defined as $Q_R = ([Q_{MF+5CB} - Q_{MF}] / Q_{MF}) \times 100$ as a function of magnetic field is calculated and plotted in Figure 5. Herein, $Q_{MF}$ and $Q_{MF+5CB}$ are the $Q$ values at a certain magnetic field for the pure MF samples and their corresponding ferro nematic material samples, respectively. Figure 5 shows that $Q_R$ increases with the applied magnetic field and tend to saturate at high field. When the externally magnetic field $B$ is less than 50 mT, the $Q_R$ is slight, while $Q_R$ becomes notable when $B$ is larger than 50 mT. Comparing with the $Q$ value of the pure MF samples, the relative enhancement of $Q$ value of the corresponding ferro nematic samples ($Q_{5CB}$) can reach about 6.8%.

To investigate the influence of 5CB concentration on the extinction coefficient and figure of merit of optical properties of the ferro nematic samples, experiments are done with samples MF-5CB, MF-5CB(2), MF-5CB(3), and MF-5CB(4), and the results are shown in Figure 6. Figure 6 shows that the extinction coefficient does not change with the field strength for a given sample and that the ferro nematic sample with higher volume fraction of 5CB has a smaller extinction coefficient.

Figure 6 also indicates that the value of $Q$ increases gradually with the applied magnetic field and tends to saturate at high field. Moreover, the higher the volume fraction of 5CB, the higher the value of $Q$ is under certain fixed field strength. Therefore, the value of $Q$ for the ferro nematic materials can be tuned by adjusting the volume fraction of 5CB.

Conclusions

The optical properties (birefringence and figure of merit of optical properties) of the pure MF and ferro nematic thin films under externally applied magnetic field are investigated. The pure MF and the ferro nematic samples show the similar magnetic-field-dependent properties of birefringence and figure of merit of optical properties, which increase with magnetic induction and tend to saturate at high field. Both types of samples with high volume fraction of magnetic particle have high bi refringence. Besides, the ferro nematic material with high volume fraction of 5CB has a relatively high value of $Q$ under a certain fixed field strength. The experimental results reveal that the magnetic particle concentration is crucial to the birefringence of the samples and that 5CB concentration has no influence on the birefringence of the samples. However, the 5CB concentration is crucial to the figure of merit of optical properties of the ferro nematic samples, and magnetic particle concentration has no influence on the figure of merit of optical properties of the ferro nematic samples. The $Q$ values of the ferro nematic materials are larger than those of their counterparts (pure MFs). The maximum relative increase in $Q$ value is around 6.8% for our experimental samples.

Abbreviations

5CB: 4-cyano-4′-pentylbiphenyl (C18H19N) nematic liquid crystal; MF: Magnetic fluid.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

The experiment measurement and data calculation of this study were mainly done by the first author, XW. SP contributed to both the theoretical and experimental work and gave some useful suggestions to XW. GY and HU contributed to experimental work and gave XW some help. This article was written by XW and revised by SP. All authors read and approved the final manuscript.

Acknowledgments

This research was supported by the Innovation Program of Shanghai Municipal Education Commission (11Y12120) and the National Natural Science Foundation of China (10774048).

References

1. Rosensweig R. Directions in ferrohydrodynamics. J Appl Phys 1985, 57:4259–4264.
2. Scherer C, Neto AM. Ferrofluids: properties and applications. Braz J Phys 2005, 35:718–727.
3. Ganguly R, Gaidh AP, Sen S, Puri BK. Analyzing ferrofluid transport for magnetic drug targeting. J Magn Magn Mater 2005, 289:331–334.
4. Pu S, Chen X, Chen Y, Liao W, Chen L, Xia Y. Measurement of the refractive index of a magnetic fluid by the retroreflection on the fiber-optic end face. Appl Phys Lett 2005, 86:171904.
5. Rakher YL, Stepanov VI. Dynamic birefringence in ferrocloids in crossed fields: interaction of magnetic and mechanical orientational degrees of freedom. Colloid J 2003, 65:65–77.
6. Cruz JL, Andres MV, Hernandez MA. Faraday effect in standard optical fibers: dispersion of the effective Verdet constant. Appl Opt 1996, 35:922–927.
7. Pu S, Chen X, Chen Y, Xu Y, Liao W, Chen L, Xia Y. Fiber-optic evanescent field modulator using a magnetic fluid as the cladding. J Appl Phys 2006, 99:093516.
8. Fang X, Xuan Y, Li Q. Measurement of the extinction coefficients of magnetic fluids. Nanoscale Res Lett 2011, 6:237.
9. Mehta RV, Patel R, Desai R, Upadhyay RV, Parekh K. Experimental evidence of zero forward scattering by magnetic spheres. Phys Rev Lett 2006, 96:127402.
10. Mehta RV, Patel R, Upadhyay RV: Direct observation of magnetically induced attenuation and enhancement of coherent backscattering of light. Phys Rev B 2006, 74:195127.

11. Yuan W, Yin C, Xiao P, Wang X, Sun J, Huang S, Chen X, Cao Z: Microsecond-scale switching time of magnetic fluids due to the optical trapping effect in waveguide structure. Microfluid Nanofluid 2011, 11:781–785.

12. Pu S, Chen X, Chen L, Lao W, Chen Y, Xia Y: Tunable magnetic fluid grating by applying a magnetic field. Appl Phys Lett 2005, 87:021901.

13. Li J, Liu X, Lin Y, Bai L, Li Q, Chen X, Wang A: Field modulation of light transmission through ferrofluid film. Appl Phys Lett 2007, 91:253108.

14. Pu S, Chen X, Di Z, Xia Y: Relaxation property of the magnetic-fluid-based fiber-optic evanescent field modulator. J Appl Phys 2007, 101:053532.

15. Chen J, Chen X, Pu S, Di Z, Xia Y: Realization of optical limiting with a magnetic fluid film. Opt Commun 2007, 276:268–271.

16. Han S, Li J, Gao R, Zhang T, Wen B: The modification effect in magnetization behaviors for CoFe2O4-p-NiFe2O4 binary ferrofluids. Appl Phys A Mater Sci Process 2010, 98:179–186.

17. Li J, Lin Y, Liu X, Wen B, Zhang T, Zhang Q, Xiao H: The modulation of coupling in the relaxation behavior of light transmitted through binary ferrofluids. Opt Commun 2010, 283:1182–1187.

18. Patel R, Upadhyay RV, Aswal VK, Joshi JV, Goyal PS: Macroscopic and microscopic structural integrity in magnetic colloids-cationic micellar solution: rheology, SANS and magneto-optical study. J Magn Magn Mater 2011, 323:849–856.

19. Patel R, Aswal VK, Upadhyay RV: Magneto-optically induced retardation and relaxation study in a mixed system of magnetic fluid and cationic micelles. J Magn Magn Mater 2008, 320:3366–3369.

20. Jarkova E, Pleiner H, Muller HW, Brand HR: Macroscopic dynamics of ferronematics. J Chem Phys 2003, 118:2422–2433.

21. Brochard F, de Gennes PG: Theory of magnetic suspensions in liquid crystals. J Phys 1970, 31:691–708.

22. Chen SH, Amer NM: Observation of macroscopic collective behavior and new texture in magnetically doped liquid-crystals. Phys Rev Lett 1983, 51:2298–2301.

23. Burylov SV, Raikher YL: Ferronematics: enhanced magneto-optical response of a liquid crystalline system. Mat Sci Eng C-Bio Mater Sen Sys 1995, 2:335–241.

24. Raikher YL, Stepanov VI: Transient field-induced birefringence in a ferronematic. J Magn Magn Mater 1999, 201:182–185.

25. Chen SH, Liang BJ: Electro-optical effect of a magnetically biased ferronematic liquid-crystal. Opt Lett 1988, 13:716–718.

26. Liang BJ, Chen SH: Electric-field-induced molecular-reorientation of a magnetically biased ferronematic liquid-crystal film. Phys Rev A 1989, 39:1441–1446.

27. Goto H, Nimori S, Akagi K: Synthesis and properties of mono-substituted liquid crystalline polyacetylene derivatives-doping, magnetic orientation, and photo-isomerization. Synthetic Met 2005, 155:576–587.

28. Matuo CY, Neta ANF: Time dependence of the magnetic grain concentration and secondary grain aggregation in ferronematic lyotropic liquid crystals subjected to magnetic field gradients. Phys Rev E 1999, 60:1815–1820.

29. Di Z, Chen X, Pu S, Hu X, Xia Y: Magnetic-field-induced birefringence and particle agglomeration in magnetic fluids. Appl Phys Lett 2006, 89:211106.

30. Pu S, Dai M, Sun G, Liu M: Linear birefringence and linear dichroism coupled optical anisotropy of magnetic fluids by external magnetic field. In In The International Symposium on Photonics and Optoelectronics (SOPO 2009); August 14–16 2009. Wuhan: Piscataway: IEEE; 2009:857–862.

31. Taketomi S: Magnetic fluids anomalous pseudo-cotton mouton effects about 10 times larger than that of nitrobenzene. J Exp Theor Phys 1983, 22:1137–1143.

32. Patel R: Mechanism of chain formation in nanofluid based MR fluids. J Magn Magn Mater 2011, 323:1360–1363.