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Magnetic field induced Fréedericksz transition of a planar aligned liquid crystal doped with metalloporphyrins FeTPPCl, MnTPPCl and ZnTPP

XIANG YING†, SHI JUE†, LIN ZIYANG†‡, LI TAO§, JIN-WANG HUANG§
and LIANG-NIAN JI§

†The Department of Physics, ZhongShan University, Guang Zhou 510275,
PR China
‡The Department of Physics, JiNan University, Guang Zhou 510632,
PR China (for mail)
§The Department of Chemistry, Zhong Shan University, Guang Zhou 510275,
PR China

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We observed that the planar aligned nematic liquid crystal (5CB) doped with a volume fraction of 1% of FeTPPCl [5,10,15,20-tetraphenylporphyriniron(III) chloride] or MnTPPCl [5,10,15,20-tetraphenylporphyrinmanganese(III) chloride] dramatically decreased the critical magnetic field for the magnetic field induced Fréedericksz transition, while 5CB doped with ZnTPP [5,10,15,20-tetraphenylporphyrinzinc(II)] revealed no such effect, when compared with pure 5CB. In the guest–host (5CB) system, FeTPPCl and MnTPPCl as guests are both strong paramagnetic materials with an interaction through coordination of the −CN group in 5CB onto the metal ion of the porphyrin. As a result, the 5CB molecules are dragged to reorientate under a static magnetic field, while ZnTPP is a diamagnetic material without such a property. This phenomenon concerning magneto-optical components could be useful in liquid crystal displays.

1. Introduction

Due to their large optical anisotropies, liquid crystals (LCs) have a large optical non-linearity which is the result of molecular reorientation (Fréedericksz transition) in an external field which exceeds the critical field. How the critical field can be decreased is very important in applications, especially for the electro-optical or magneto-optical effects of LC components. In 1970 Brochard and de Gennes first proposed a theory [1] of magnetic suspensions (ferronematics) in which the LC could be doped with small magnetic grains. The applied magnetic field would change the orientation of the grains, and through mechanical coupling between the magnetic grains and the LC, the grains would drag the LC molecules to reoriente. Hence, the presence of the magnetic grains enhances the magnetic susceptibility of the doped LC. Many experiments were performed and confirmed this prediction [2]. In this paper, we report another kind of doped LC, using a paramagnetic ion dopant.

We first observed that planar aligned 5CB doped with FeTPPCl or MnTPPCl shows a dramatically decreased critical magnetic field for twist reorientation in a static magnetic field, compared with pure 5CB. For a 19.2 μm thick sample, a volume fraction of 1% of FeTPPCl [5,10,15,20-tetraphenylporphyriniron(III) chloride] decreased the critical magnetic field from 3600 to 600 gauss, while the same fraction of ZnTPP [5,10,15,20-tetraphenylporphyrinzinc(II)] displayed no such effect.

The doped LCs studied here have several differences from conventional ferronematics: (a) the dopant (guest) and LC (host) form a uniform solution, while the ferronematics are suspensions; (b) the coupling here between the guest and host is at a molecular level (coordination bond) rather than a colloidal level (mechanical force); (c) the dopant used is a paramagnetic material instead of magnetic grains. Compared with the difficulty in obtaining a well aligned suspension, we can easily change to a different dopant and via the magnetic-induced Fréedericksz transition of the doped LC, we can study the dopant's magnetic properties and the molecular coupling between the guest and host.

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The Frank continuum elastic theory and a dipole model are used to describe the distribution of the director twist reorientation angle in the magnetic field, and Berreman's '4 × 4' optical matrix is used to calculate the light transmission in the LC layer. The results of the calculation are in good agreement with the experimental results.

2. Experimental arrangment and theory

The molecular structures of 5CB, FeTPPCl, MnTPPCl and ZnTPP are shown in figure 1 [3]. Four samples were studied in the experiments; they were 5CB, 5CB doped with 1% volume fraction of FeTPPCl, 5CB doped with 1% volume fraction of MnTPPCl, and 5CB doped with 1% volume fraction of ZnTPP. The samples of FeTPPCl, MnTPPCl and ZnTPP were synthesized by standard methods. The samples were sandwiched between two glass substrates with $19.0\,\mu\mathrm{m}$ spacers; the two glass substrates were coated with polyimide and rubbed unidirectionally to give planar alignment. Since the Fe(III), Mn(III) and Zn(II) as guests have some interaction with the host in the form of coordination of the −CN group in 5CB to the metal ion of the porphyrin, the 5CB molecules lie perpendicular to the plane of the metalloporphyrin. The alignment of the guest molecules in the planar aligned host (5CB) is illustrated in figure 2. ESR indicated that FeTPPCl is a strong paramagnetic material, and the corresponding $g_\perp$ and factor $g_\parallel$ factors are 6.0 and 2.0, respectively. For MnTPPCl, $g_\perp = 5.6$ and $g_\parallel = 2.0$. In a magnetic field, the FeTPPCl or MnTPPCl molecules will drag the LC molecules to reorientate, which makes a great contribution to the decrease of the critical field. For ZnTPP, there is no contribution to the decrease of the critical field.

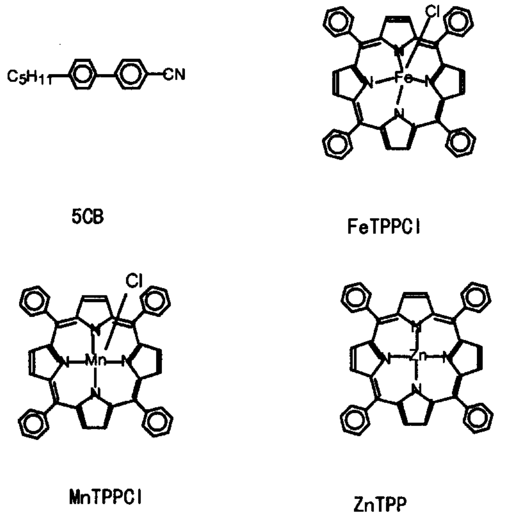

Figure 1. The molecular structures of the liquid crystal host and the metalloporphyrins.

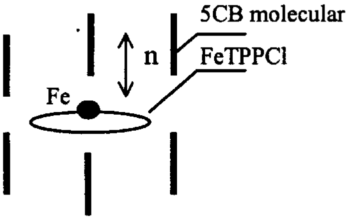

Figure 2. The alignment of the guest–host system (**n** is the director orientation of the LC).

The experimental arrangement is shown in figure 3 with the temperature stabilized at 25°C. Optical phase retardation was used to probe the varying light transmission induced by the twist reorientation in the external field. As the wavelength ranges of light absorption of FeTPPCl, MnTPPCl and ZnTPP are all shorter than $0.6\,\mu\mathrm{m}$, with the absorption peaks at $0.42\,\mu\mathrm{m}$ and $0.514\,\mu\mathrm{m}$, we can use a $\lambda = 0.6328\ \mu\mathrm{m}$ He-Ne laser as the probe light. The He-Ne laser as the probe beam is polarized at 45° to the Y-axis, and is normally incident to the sample along the Z-axis; d is the thickness of the sample. The orientation of the director $\mathbf{n}_0$ (unperturbed) is along the Y-axis and the magnetic field H is along the X-axis. With an analyser (P2) crossed with the polarizer (P1), the output light is measured by the photodetector. When the magnetic field H is larger than the critical magnetic field H_C, the LC molecules will be reorientated, which induces the varying output light, and the molecular reorientation angle $\theta(z)$ is in the XY plane.

Although the Mauguin adiabatic theorem [4] indicates that polarized light is not suitable for probing the twist reorientation, its valid condition is $(n_\parallel - n_\perp)d \gg \lambda$, where $n_\parallel$ and $n_\perp$ are the refractive indices parallel and perpendicular to the director, respectively. Regarding the configuration in this paper, both experiment and calculation show that it is valid to use polarized light.

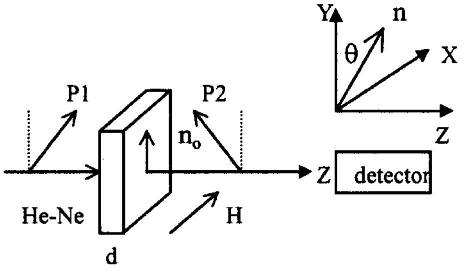

Figure 3. The experimental arrangement.

2.1. *For $H = 0$*

There is no reorientation in the LC layer, the director is parallel to the Y-axis and the layer is uniaxial anisotropic; the output light transmission T can be written as:

$$T = \sin^2 \frac{(n_\parallel - n_\perp)d}{\lambda}\pi. \qquad (1)$$

2.2. *For $H > H_C$*

There is a twist reorientation in the LC layer. As the metal ion in the dopant and the $-$CN group in 5CB form a coordination bond, with the strong coupling approximation, we simply regard the dopant as a magnetic dipole and its direction is colinear with the LC director **n** [1]; therefore the Euler–Lagrange equation may be expressed as [5]:

$$K_{22}\frac{\mathrm{d}^2\theta}{\mathrm{d}z^2} + \chi_a H^2 \sin\theta\cos\theta + C\mu H\cos\theta = 0 \qquad (2)$$

where K_{22} is the twist elastic constant and $\chi_a = \chi_\parallel - \chi_\perp$, with $\chi_\parallel$ and $\chi_\perp$ being the diamagnetic susceptibilities parallel and perpendicular to the director, respectively. C is the concentration of dopant and μ is the dipole moment per unit volume; for 5CB and ZnTPP, $\mu = 0$.

Due to the reorientation, the LC layer is an inhomogenous medium, and the Berreman '4×4' optic matrix [6, 7] was used to calculate the light transmission T, as a function of the twist angle $\theta(z)$.

3. The experiment and calculation of results

When $H = 0$, from equation (1) the light transmission of the sample is $T = 0.5$, from which the accurate thickness $d = 19.2\,\mu$m can be obtained. The critical magnetic field for the twist reorientation can be determined by increasing the magnetic field. The measured T versus H for various samples are in figure 5 and show that the critical magnetic fields of 5CB, 5CB doped with 1% of ZnTPP, 5CB doped with 1% of MnTPPCl and 5CB doped with 1% of FeTPPCl are 3600, 3450, 2000 and 600 gauss, respectively.

Assuming the cell thickness is $d = 19.2\,\mu$m, $K_{22} = 5 \times 10^{-12}$ N and $\chi_a = 1$, we chose the doping coefficients $C\mu = 0.76$ J T m^{-3} (FeTPPCl) and $C\mu = 0.15$ J T m^{-3} (MnTPPCl) in order to simulate the experimental results. The molecular twist angles $\theta(z)$ under a static magnetic field have been theoretically acquired by numerical calculation using equation (2); these are shown in figure 4. The calculation for 5CB doped with 1% of FeTPPCl and MnTPPCl are in good agreement with the measurements. Although FeTPPCl and MnTPPCl have similar properties, they have different effects on the decrease of the critical magnetic field. This may be because the interaction between the Mn(III) in MnTPPCl and the $-$CN group in 5CB is different from the interaction between Fe(III) and the $-$CN group, and this is not taken into account in our simple model.

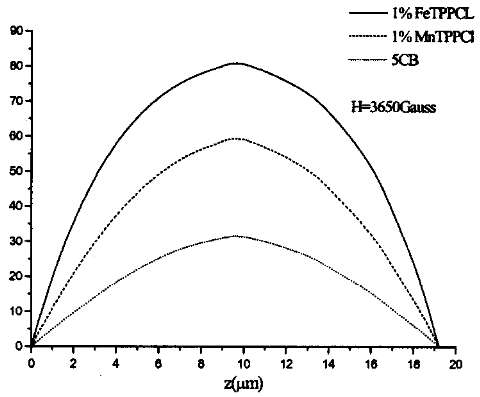

Figure 4. The twist angle $\theta(z)$ under a magnetic field for various samples.

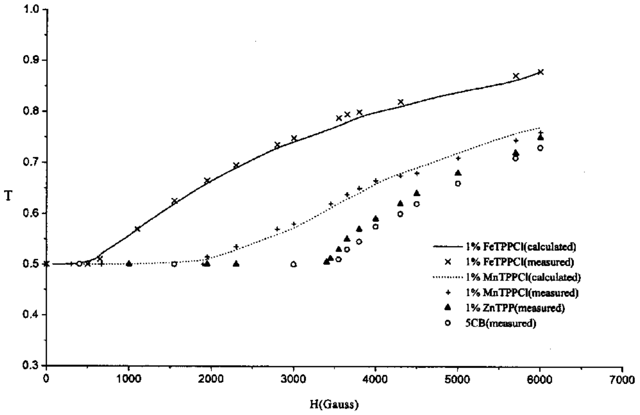

Figure 5. Light transmission T vs. magnetic field H for various samples.

4. Conclusion

The experiments indicate that a low concentration of dopant in a planar aligned LC will dramatically decrease the critical field for twist reorientation in a static magnetic field, which is very useful in the study of optical non-linearities in magnetic fields. The dopants should have some coupling with the LC molecules and have strong magnetic anisotropy. FeTPPCl and MnTPPCl are revealed to possess such properties.

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