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A Homeotropical Alignment Nematic Liquid Crystal Doped with FeTPPCl Will Dramatically Decrease the Critical Magnetic Field for the Bend Reorientation in a Static Magnetic Field

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The Freedericksz transition of homeotropical alignment liquid crystal doped with little FeTPPCl, which was induced by a perpendicular dc magnetic field, has been studied theoretically and experimentally in this paper. And the doped 5CB was observed to have dramatically decreased the critical magnetic field for bend reorientation, only one fourth of that needed for pure 5CB. This phenomenon is due to the intense paramagnetic of FeTPPCl [5,10,15,20-Tetraphenylporphineiron(III) chloride] and the interaction between the host and guest in the form of the coordination of -CN in 5CB onto the metal ion of the porphyrino. However, 5CB doped with ZnTPP [5,10,15,20-Tetraphenylporphinez-inc(II)] exhibited no decrease in the critical magnetic field. This result is very useful in liquid crystal display as magneto-optic component.

Keywords: Liquid Crystal; homeotropical; magnetic; transition; FeTPPCl

INTRODUCTION

The critical magnetic field (H_C) is very important for the liquid crystal (LC) device, for only magnetic field exceeding the H_C can make the LC reorientate, which induce the optical nonlinearity. Usually, H_C is up to several thousand

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gauss for device of ten micrometers thick, which is very difficult in application. In 1970 Brochard and de Gennes firstly proposed a theory[1] of magnetic suspensions (ferronematics) in which LC could be doped with small magnetic grain. The applied magnetic field changed the orientation of the grains, through mechanical coupling between the magnetic grains and LC, the grains will drag the LC molecular to reorientation. Hence, the presence of the magnetic grain enhanced the magnetic susceptibility of doped LC. Many experiments were performed and proved this prediction [2]. In this paper, we report another kind of doped LC, LC doped with paramagnetic ion dopant. The experiment showed a homeotropic alignment LC (5CB) doped with FeTPPCl [5,10,15,20-Tetraphenylporphineiron(III) chloride] will dramatically decrease the critical magnetic field for bend reorientation, compared to the pure 5CB. For comparison, the 5CB doped with ZnTPP [5,10,15,20-Tetraphenylporphinezinc(II)] has also been studied and revealed no positive effect on the decrease of critical magnetic field. The doped LC used here and the conventional ferronematics have several differences: (a) The dopant (guest) and LC(host) here have formed a uniform solution while the ferronematics were suspension. (b) The coupling between the guest and host here is at a molecular level(coordination bond) rather than a colloidal level(mechanical force). (c) The dopant we used is a paramagnetic material instead of magnetic grain. Compared to the difficulty of a well-aligned suspension, we can easily change the different dopant and via the magnetic-induced Freedericksz transition of doped LC, we could study the dopant's magnetic property and the molecular coupling between the guest and host.

EXPERIMENTAL ARRANGMENT AND THEORY

The samples used are sample A(5CB doped with 1% concentration in weight of FeTPPCl), sample B(5CB doped with 0.6% concentration in weight of FeTPPCl), sample C (5CB doped with 1% concentration in weight of ZnTPP) and sample D(5CB). The FeTPPCl and ZnTPP are synthesized by standard methods, with the molecular structure shown in Fig.1[3]. The samples were sandwiched by two glass substrates with 14.5μm spacer, the two glass substrates were coated with DMOAP(octadecyldimethyl[3-(trimethoxysilyl)-ropyl]ammoniumchloride), which induced the homeotropic alignment at surface. 5CB and dopant form a host-guest system, which possesses interaction between the coordination of-CN in 5CB and the metal ion of the porphyrino. Usually, the interaction is the strongest when 5CB molecules are perpendicular to the plane of FeTPPCl. As for 5CB molecular, the $^{\alpha}C$ is sp hybridized, the angle of -C≡N : is about 180°(the ":" denoted the isolated electrons of N atom), which forms coordination bond with

Fe atom in FeTPPCl. And that the coordination bond energy is lower and the coupling is weaker when the 5CB molecule is parallel to the plane of FeTPPCl. So we concluded that 5CB molecules lie perpendicular to the plane of FeTPPCl, which may be illustrated in Fig.2. FeTPPCl is a paramagnetic material, and it's $g_{//}$ and $g_{\perp}$ factor obtained from ESR are 6.0 and 2.0, respectively. In magnetic field, the FeTPPCl molecules will drag the LC molecules to reorientate, which make great contribution to the decrease of H_C. Since ZnTPP is a diamagnetic material, it can't make any contribution to the decrease of H_C.

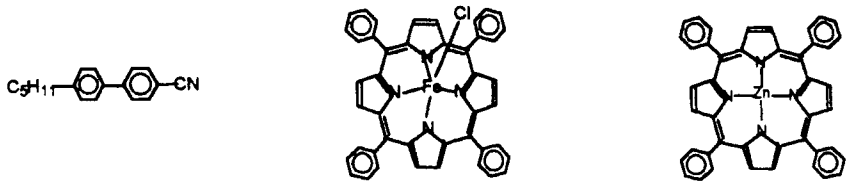

FIGURE 1 The molecular structures of Liquid Crystal and metalloporphyrins

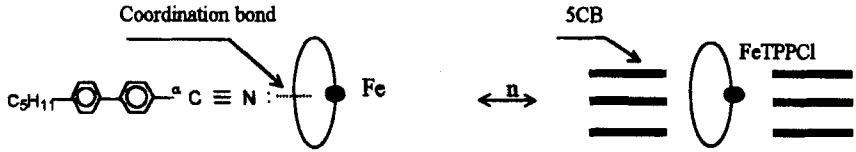

FIGURE 2 The alignment of the guest-host system (n is the director orientation of LC)

Let Z axis be the sample surface normal and θ be the molecular reorientation angle from Z axis, the magnetic field **H** is applied along X axis. The director **n**and **H** are expressed as **n**=[sinθ(z),0,cosθ(z)] and **H**=(H,0,0), respectively. As the Fe ion in FeTPPCl and -CN in 5CB formed a coordination bond, applying the strong coupling approximation, we simply regard the dopant as a magnetic dipole moment and it's direction is colinear to the LC director **n**[1]. the Euler-Lagrange equation may be written as follow[4]:

$$(K_{11}\sin^2\theta + K_{33}\cos^2\theta)\frac{d^2\theta}{dz^2} + (K_{11} - K_{33})\sin\theta\cos\theta\left(\frac{d\theta}{dz}\right)^2 + \chi_a H^2 \sin\theta\cos\theta + \mu H\cos\theta = 0 \quad (1)$$

Where K_{11}, K_{33} are elastic constant, and $\chi_a=\chi_{//}-\chi_{\perp}$, with $\chi_{//}$ and $\chi_{\perp}$ being the diamagnetic susceptibilities parallel and perpendicular to the director, respectively. μ is the dipole moment per unit volume, which is a constant when magnetic field is changed but associates with the dopant and concentration, i.e., for 5CB and ZnTPP, $\mu=0$.

The molecular reorientation of LC is probed by the optic phase retardation technique at temperature of 25°C[5] : a He-Ne laser beam polarized at 45° to the magnetic field is normally incident to the samples. The molecular reorientation in the X-Z plane which change the refractive index n_{eff} of e ray. Thus, with an analyzer crossed with the polarizer, the output light transmission T is:

$$T = \sin^2\left(\frac{\delta}{2}\right)$$

$$\delta = \frac{2\pi}{\lambda}\int_0^d [n_{eff}(z) - n_o]dz \qquad (2)$$

$$n_{eff} = \left[\frac{\cos^2\theta}{n_o^2} + \frac{\sin^2\theta}{n_e^2}\right]^{-1/2}$$

Where δ is the phase retardation between the o beam and e beam after the probe beam traversing the sample, d is the thickness of the samples. As the absorbing range of FeTPPCl and ZnTPP are shorter than 0.6μm with the absorbing peak in 0.42 μm and 0.51μm, the 0.63μm He-Ne laser can be used as probe light.

RESULTS

The measured and calculated light transmission T versus the magnetic field H for samples are shown in Fig.3, which show the H_C of samples are 1500 gauss, 3500 gauss, 6000 gauss and 6100 gauss respectively. The doped LC displays rather flat transition curve, compared to the pure LC. The calculated results are in good agreement with the measurement, which give $\mu=0.38$ for sample A (doped 1.0% FeTPPCl) and $\mu=0.15$ for sample B (doped 0.6% FeTPPCl). Actually, the μ is not only related to the concentration but also related to the interaction between the host and guest, which is not considered in our rough model.

Since so little dopant will dramatically decrease the critical magnetic field H_C for Freedericksz transition, the dopant should has some interaction with the LC molecules and has an intense magnetic effect. The experiment has also indicated that the concentration of dope has significant influence on the H_C.

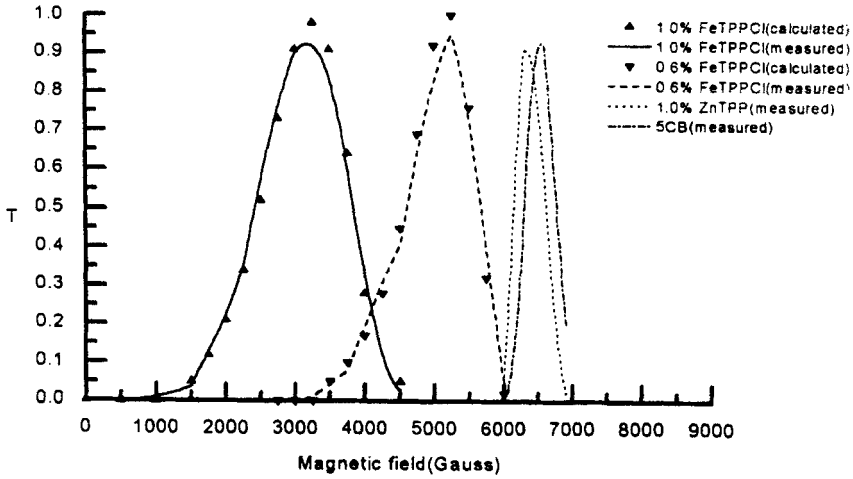

FIGURE 3 The light transmission T(measured and calculated) vs. magnetic field for various samples

Acknowledgements

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