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Preliminary communication

Magnetic-field-induced Fréedericksz transition of a planar aligned liquid crystal doped with porphyrinatozinc(II): influence of the substituent of the porphyrin ring

TAO LI, XIANG YING[†], LONG-PEI SHI[†], JIN-WANG HUANG*,
 LIN ZIYANG^{†‡}, JUE SHI[†] and LIANG-NIAN JI

Department of Chemistry, ZhongShan University, GuangZhou 510275, PR China

[†]Department of Physics, ZhongShan University, GuangZhou 510275, PR China

[‡]Department of Physics, Jinan University, Guangzhou 510632, PR China

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The magnetic-field-induced Fréedericksz transition of a planar aligned nematic liquid crystal doped with 1.0 wt % of a diamagnetic porphyrinatozinc(II) has been studied. It was observed that 5CB doped with 1.0 wt % of derivatives of Zn(II)TPP—5,10,15,20-tetraphenylporphyrinatozinc(II)—which have different substituents in one phenyl ring display sharp Fréedericksz transition curves and dramatically decrease the critical magnetic field compared with pure 5CB.

Porphyrins are structurally related to important biological substances (heme, chlorophyll and petroleum). Extensive studies have been conducted on the physico-chemical properties of porphyrins and their metal derivatives [1]. Recently we have reported the magnetic-field-induced Fréedericksz transition of a planar aligned liquid crystal doped with the paramagnetic dopants Fe(III)TPPcI and Mn(III)TPPcI [2]. In this paper we present preliminarily results about another kind of doped LC; here the LC is doped with diamagnetic dopants, substituted derivatives of Zn(II)TPP, which also dramatically decrease the critical magnetic field. The experiment shows that longer substituents give a the larger diamagnetic susceptibility anisotropy. Furthermore, Frank continuum elastic theory is applied to describe the distribution of the director twist reorientation angle, and Berreman's '4 × 4' optical matrix is used to calculate the light transmission in the LC layer. The calculations give results in good accordance with experimental results.

The derivatives of porphyrinatozinc(II) were synthesized according to a previously published method [3]. The molecular structures are shown in figure 1. Five samples studied consisted of 5CB, 5CB doped with 1.0 wt % of Zn(II)TPP, Zn(II)(*o*-BzTaBuTPP)—{5-[4-(*o*-benzothiazolethio)butoxy]phenyl-10,15,20-tri(*p*-methylphenyl)porphyrinatozinc(II)}, Zn(II)-

(*o*-ImPeTPP)—{5-[*o*-(imidazole)pentyl]phenyl-10,15,20-triphenylporphyrinatozinc(II)} or Zn(II)-(*o*-ImPrTPP)—{5-[*o*-(imidazole)propoxy]phenyl-10,15,20-triphenylporphyrinatozinc(II)}. The samples were sandwiched between two glass substrates with a 19.0 μm spacer; the two glass substrates were coated with polyimide and rubbed unidirectionally to obtain planar alignment.

The molecular reorientation of the LC was probed by the optical phase retardation technique at a temperature of 28°C [4, 5]. The optical set-up is shown in figure 2. As the absorption spectra of Zn(II)TPP, Zn(II)(*o*-BzTaBuTPP), Zn(II)(*o*-ImPeTPP) and Zn(II)-(*o*-ImPrTPP) show that the absorbing range is from 0.38 to 0.46 μm, with the absorption peak at 0.42 μm and no absorption at 0.6328 μm, a He-Ne Laser (0.6328 μm) can be used as the probe light. The probe laser beam polarized at 45° to the *y* axis is incident normally to the sample, along the *z* axis, and *d* is the thickness of the sample (measured *d* = 19.2 μm). The orientation director *n*₀ (unperturbed) is along the *y* axis and the magnetic field **H** is along the *x* axis. With an analyser (P2) perpendicular to the polarizer (P1), the output light is probed by the photodetector. When the magnetic field **H** is larger than the critical magnetic field **H**_c, the LC molecules possess different twist angles $\theta(z)$ (lying in the *x*-*y* plane) as a function of the direction *z*, except for the surface molecules, which still align along the direction *y*. After propagating through the LC

* Author for correspondence, e-mail: cesjln@zsu.edu.cn

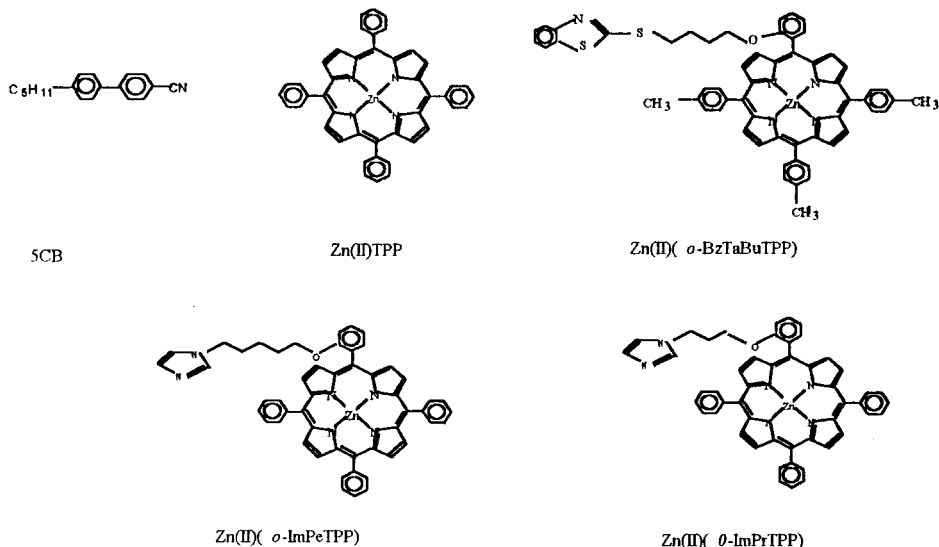


Figure 1. The molecular structures of the liquid crystal and the porphyrinatozinc(II) complexes.

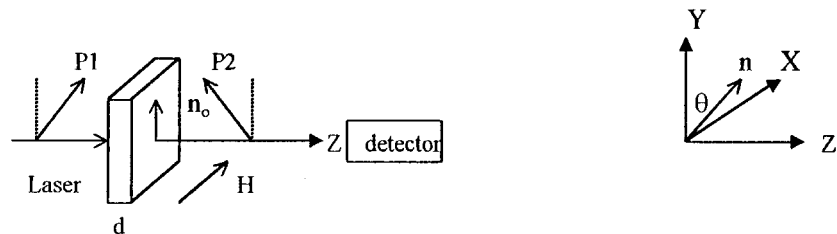


Figure 2. The experimental set-up.

layer, the incident light becomes elliptically polarized and through P2 the exit light intensity is measured by the detector.

For a dopant with an induced diamagnetic susceptibility anisotropy [6], under the strong coupling approximation, we give the Euler–Lagrange equation as follows:

$$K_{22} \frac{d^2 \theta}{dz^2} + (\chi_a \mathbf{H}^2 + C\chi_d \mathbf{H}^2) \sin \theta \cos \theta = 0 \quad (1)$$

where K_{22} is elastic constant, χ_a , χ_d are the diamagnetic susceptibility anisotropies per unit volume of 5CB and dopant, respectively, and C is the concentration of the dopant.

Considering now the results, the experimental and theoretical light transmissions T as functions of the magnetic field \mathbf{H} for the various samples are shown in figure 3. The corresponding \mathbf{H}_c and χ_d values are shown in the table. The order of decreasing \mathbf{H}_c obtained from the experiments is:

$$\begin{aligned} 5\text{CB} &> 5\text{CB-Zn(II)TPP} > 5\text{CB-Zn(II)}(o\text{-ImPrTPP}) \\ &> 5\text{CB-Zn(II)}(o\text{-ImPeTPP}) \\ &> 5\text{CB-Zn(II)}(o\text{-BzTaBuTPP}). \end{aligned}$$

Table 1. The values of \mathbf{H}_c and χ_d for different samples.

Sample	\mathbf{H}_c/T	χ_d
5CB	0.36	1
ZnTPP	0.35	—
Zn(II)(<i>o</i> -ImPrTPP)	0.29	50
Zn(II)(<i>o</i> -ImPeTPP)	0.24	120
Zn(II)(<i>o</i> -BzTaBuTPP)	0.17	300

The order of increasing χ_d obtained from the calculations is:

$$\begin{aligned} \text{Zn(II)}(o\text{-ImPrTPP}) &< \text{Zn(II)}(o\text{-ImPeTPP}) \\ &< \text{Zn(II)}(o\text{-BzTaBuTPP}). \end{aligned}$$

It is obvious that the substituent linked to the porphyrin ring plays an important role in determining the magnitude of the induced diamagnetic susceptibility anisotropy, and that the longer the substituent is, the larger is χ_d .

As we suggest in a previous report [2], metalloporphyrins and 5CB form a guest–host system, and there

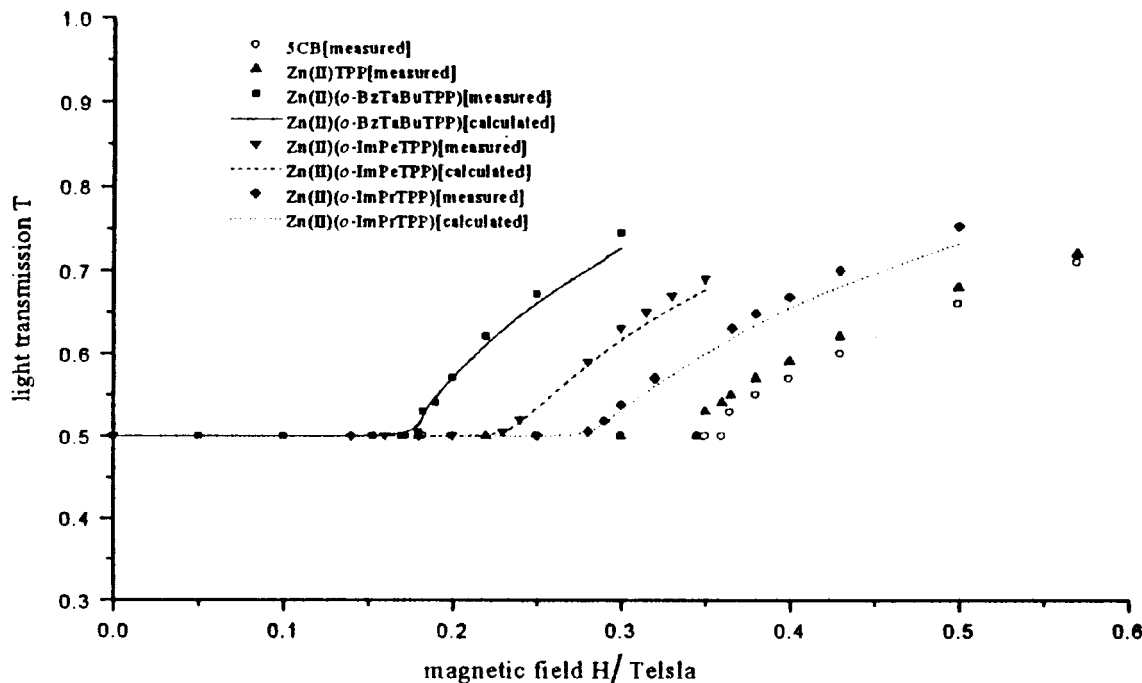


Figure 3. The Fréedericksz transition of the different samples.

is an interaction between the host and guest in the form of coordination of the $-\text{CN}$ in 5CB to the Zn ion of the porphyrin. The guest porphyrins $\text{Zn(II)}(o\text{-BzTaBuTPP})$, $\text{Zn(II)}(o\text{-ImPeTPP})$ and $\text{Zn(II)}(o\text{-ImPrTPP})$ have much larger diamagnetic susceptibility anisotropies and will drag the 5CB molecules into reorientation under lower magnetic fields.

Considering the differences in the magnetic-field-induced Fréedericksz transition of the liquid crystal doped with different dopants, it seems that this method could be used to determine the magnetic properties of a dopant.

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