Diffraction efficiency and *I–V* characteristics of metal-free phthalocyanine doped nematic liquid crystals

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ABSTRACT

The synthesis and characterization of the tetra-4-benzyloxyphenoxy substituted metal-free phthalocyanine (H_2Pc) is reported for the first time. Formation of the photoinduced gratings has been experienced in a metal-free phthalocyanine doped nematic liquid crystal (LC) system and its *I–V* properties are characterized by electrical measurements. Four samples are prepared at different doping percentages and in homogenously aligned sandwiched geometry. We report the results of two set of experiments on these samples. One of them is the grating diffraction experiment for the analysis of optically induced reorientation process which is a basis for possible holographic applications. Accessible diffraction efficiency is found to be linearly increasing as the amount of the phthalocyanine doping rises. In the scope of the other set of measurements *I–V* peculiarity of the system is also found to be enhanced and linearly dependent on doping.

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1. Introduction

Liquid crystals (LC) are highly nonlinear optical materials due to their sensitive property, activating under even relatively low optical fields. Several nonlinear mechanisms investigated so far have revealed the promising characters of these materials. The difference in refractive indices, for fields polarized along, and perpendicular to, the director axis brings about a large birefringence property, which is an opportunity for various applications [1]. The photorefractive (PR) effect of LCs attracts much interest for holographic data storage due to their extremely large change of refractive index that can be induced by a laser. Nematic liquid crystals are also well known for their nonlinear optical (NLO) properties associated with laser induced director axis reorientation effects [2]. It is possible to enhance the optical nonlinearity in LC by doping pigments, dyes, nano-particles etc., and principally different reorientation mechanisms can take place depending upon mainly the doping based circumstances. These mechanisms are discussed in several research papers such as [3]. In brief, in the explanation of dye enhanced reorientation mechanism the starting point is the interaction between LC molecules and the excited dye molecules. It is assumed that

the mean fields acting on the dye molecules are different when the dye molecules are in their ground state and when they are in their excited state. This assumption brings about a modified version of optical torque, if the dye molecules are in their excited state; this means that angular momentum of dye molecules are increased by pumping laser. That is why host molecules behave in the way of minimizing their angular momentum so that total angular momentum should be conserved and this could be realized by LC molecules' reorientation. Actually this effect is known as Janossy effect [4,5]. Trans–cis photoisomerization is another mechanism which is dominant in azo dyes, in which the absorbance of light by dye molecules causes these molecules to become V shaped with ~120°. This spatial change of dye molecules reinforces the molecular orientation of neighbor LC molecules by frictional forces [6,7]. Another mechanism is the so called Photorefractive-like reorientation, in which photo-excited dopants bring about the formation of space-charge complexes, and their induced fields force the molecules to reorient by enhancing the photoconductivity [8,9]. Although the scope of this work is fundamentally devoted to experimental optimization of a new synthesis in possible LC combinations and applications rather than precise and definite explanations of molecular mechanisms, the phthalocyanines (Pcs) used in our research contributes via this photorefractive-like effect in our point of view.

Phthalocyanines are also interesting materials, which exhibit high thermal and chemical stability as well as high optical absorp-

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tion in the visible range. Due to their blue or green colour, the phthalocyanines were largely used in industry as dyes [10], and more recently due to their semiconducting properties they have proven their applicability in electronic devices such as organic photovoltaic cells and organic light emitting diodes. They are also used in optical recording and optical display devices [11,12].

In this paper, we report on the syntheses of the tetra-4-benzyloxyphenoxy substituted metal-free phthalocyanine (Scheme 1). The new compound was characterized by elemental analysis, FT–IR, ^{1}H NMR spectroscopy, electronic spectroscopy and mass spectra. The character of the prepared systems was investigated in terms of the diffraction signals depending on applied DC voltage using two wave mixing experiment. We measured diffraction efficiency for pure E7 and E7/H$_2$Pc samples doped at different percentages. Contribution of the H$_2$Pc to *I–V* character of the system was also monitored by Keithley 4200 Semiconductor Characterization System.

2. Experimental

2.1. Materials

Dimethylsulphoxide (DMSO), chloroform (CHCl$_3$), dichloromethane (DCM), tetrahydrofuran (THF), toluene, ethanol, dimethylformamide (DMF) and 2-(dimethylamino)ethanol were dried as described in Perrin and Armarego [13]. 4-Benzyloxyphenol and 2-(dimethylamino)ethanol were purchased from Aldrich. E7 was purchased from Merck. Column chromatography was performed on silica gel 60 (0.04–0.063 mm) and preparative thin layer chromatography was performed on silica gel 60 P F$_{254}$ 4-nitrophthalonitrile (1) [14] and 4-(4-benzyloxyphenoxy)phthalonitrile(2) [15] were synthesized and purified according to literature procedure.

2.2. Equipment and measurements

Elemental analyses were obtained with a Thermo Finnigan Flash 1112 Instrument. Infrared spectrum in KBr pellets was recorded on a Bio-Rad FTS 175C FT–IR spectrophotometer. Optical spectra in the UV-visible region were recorded with a Schimadzu 2001 UV Pc spectrophotometer using 1 cm path length cuvettes at room temperature. Fluorescence excitation and emission spectra were recorded on a Varian Eclipse spectrofluoremeter using 1 cm pathlength cuvettes at room temperature. The mass spectrum was acquired on a Bruker Daltonics (Bremen,Germany) MicrOTOF mass spectrometer equipped with an orthogonal electrospray ionization (ESI) source. The instrument was operated in positive ion mode using a *m/z* range of 50–800. The capillary voltage of the ion source was set at 6000 V and the capillary exit at 190 V. The nebulizer gas flow was 3 bar and drying gas flow 10 L min^{-1}. The drying temperature was set at 200 °C. ^{1}H NMR spectrum was recorded in CDCl$_3$ solutions on a Varian 500 MHz spectrometer.

Four measurement cells, whose thicknesses are 9 μm, were produced. These cells were made up of two conductive glass plates (ITO) with homogenous alignment. One of them contains pure E7 which is purchased from Merck. Actually E7 is a famous room temperature nematic LC composed from four namatogens (51% K15, 25% K21, 16% M24 and 8% T15). Molecular structures of the sample components are depicted in Fig. 1. The other three cells were filled with metal-free phthalocyanine (H$_2$Pc) at different percentages as E7/H$_2$Pc 5% (w/w), E7/H$_2$Pc 10% (w/w), E7/H$_2$Pc 15% (w/w). This H$_2$Pc was synthesised at the Department of Chemistry, Gebze Institute of Technlohgy, following the procedure described below (Section 2.3), and was mixed with the nematic LC under the ultrasonic effect. Pure E7 and H$_2$Pc doped liquid crystals were both injected into sample the cells by capillary action at room temperature.

An experimental arrangement for the two-wave mixing is schematically shown in Fig. 2(a). It consists of a He–Ne (λ = 632.8 nm) pumping source and this source is split into two components having approximately equal power by a beam splitter. Polarization of laser is arranged to be parallel to preliminary orientation of LC molecules. This polarization is actually the dominant light-molecule interaction case. The color of the doping materials is appropriate for efficient absorbance to happen at the characteristic wavelength of He–Ne laser around 632 nm. Pumping beams, having 10 mW power, were intersected on the sample with, θ = ~1^0 that makes grating constant Λ to be 36 μm and since $\Lambda^2 \gg \lambda d$, diffraction is considered to be in the Raman-Nath regime.

2.3. Synthesis

A solution of 4-(4-benzyloxyphenoxy)phthalonitrile(2) (2.00 g, 6.13 mmol) in 5 ml dry 2-(dimethylamino)ethanol (DMAE) was refluxed under argon atmosphere for 18 h. After cooling, the solution was dropped in the ethanol. The green solid
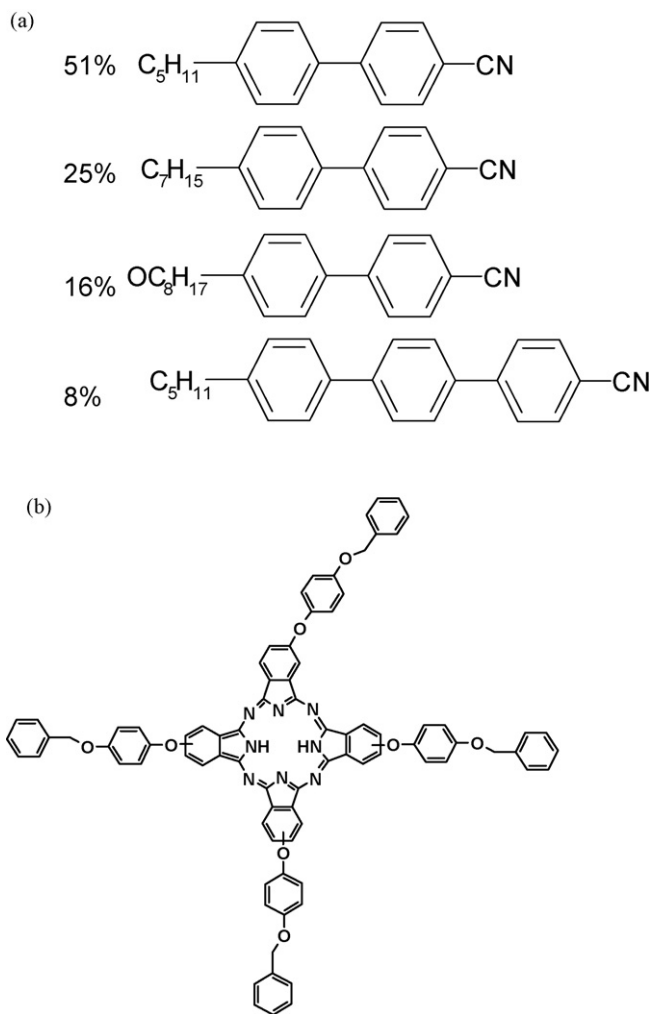

Fig. 1. Molecular structures of the samples; (a) nematic host E7 (b) metal-free phthalocyanine (H$_2$Pc).

product was precipitated and collected by filtration and washed with ethanol. The crude product was dissolved in CH$_2$Cl$_2$ and then filtered. After filtering and concentrating, the dark green waxy product was purified by passing through a silica gel column, using THF as the eluting solvent. Furthermore this product was purified with preparative thin layer chromatography (silica gel) using CHCl$_3$ as solvent system. Yield: 0.84 g (42%). UV–vis (chloroform): λ_{max} nm (log ε) 338 (4.77), 606 (4.40), 639 (4.60), 668 (4.96), 703 (5.02). IR [(KBr) $\nu_{max,}$ cm^{-1}]: 3294 (NH), 3054 (Ar–CH), 3025 (Ar–CH), 2963–2850 (CH$_2$), 1502 (C=C), 1223 (C–O–C). ^{1}H NMR (CDCl$_3$): δ, ppm 7.28 (28H, br, Pc-H, phenyl-H), 6.70–6.92 (20H, m, phenyl-H), 4.76 (8H, s, CH$_2$), 1.29 (2H, br, NH). Calc. for C$_{84}$H$_{58}$N$_8$O$_8$: C 77.17, H 4.47, N 8.57; found: C 77.46, H 4.61, N 8.05. MS (ES–MS): *m/z* (%) 1306 [M + H]$^+$.

3. Results and discussion

3.1. Synthesis and characterization

Generally, substituted phthalocyanines are prepared by cyclotetramerization of substituted phthalonitriles or 1,3-diimino-1H-isoindoles. 2(3),9(10),16(17),23(24)-tetra-substituted phthalocyanines can be synthesized from 4-substituted phthalonitriles while 1(4),8(11),15(18),22(25)-tetra-substituted phthalocyanines are obtained from 3-substituted analogues [16]. Octasubstituted phthalocyanines can be synthesized from 4,5-dichlorophthalonitriles [17]. In both cases for tetra-substituted phthalocyanines, a mixture of four possible structural isomers are obtained. The four probable isomers can be designed by their