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Polarized electroluminescence of a discotic mesogenic compound

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Polarized electroluminescence is observed for a uniaxially aligned sample of a discotic compound in its crystalline state. The alignment was achieved by coating the ITO anode with an aligned film of poly(tetrafluoroethylene) (PTFE) deposited using the friction method. Organic light emitting devices with the layer sequence glass/ITO/PTFE/tetraethyl perylene-3,4,9,10-tetracarboxylate (55 nm)/aluminium (100 nm) show linearly polarized emission of light with a dichroic ratio up to 3.2.

1. Introduction

Both liquid crystal displays (LCDs) and organic light emitting diodes (OLEDs) can be used to build full colour flat panel imaging devices [1]. In LCDs, the optical axis of a birefringent fluid is reoriented by external electric fields in order to modulate the intensity of the transmitted light. In OLEDs, however, very thin layers of organic semiconductors and luminescent dyes are used to convert electrical energy directly to emitted light. In spite of the competition of these two different techniques, it has been recognized during recent years that thin layers of suitable liquid crystalline materials might be quite useful for electroluminescent applications. Columnar liquid crystals which consist of disk-shaped organic molecules, can exhibit charge carrier mobilities along the columnar axis as high as $0.1\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$, or even larger [2–4]. This unusually high charge carrier mobility makes them suitable as charge transport layers for electroluminescent samples [5–7]. They can also serve as the luminescent component if the molecular core is a chromophore with high quantum efficiency [8–10].

Unfortunately, it is generally difficult to achieve a uniform alignment of columnar liquid crystals. However, calamitic liquid crystals which consist of rod-like molecules, can easily be aligned. Like conjugated polymers [11, 12], calamitic liquid crystals can be applied to achieve polarized electroluminescence [13–19]. Linearly polarized emission has been demonstrated for liquid crystal polymers [13, 14], low molar mass liquid crystals [15, 16], and networks obtained from reactive mesogenic monomers [17, 18]. The latter can be aligned and subsequently polymerized *in situ*. The degree of polarization can be described by the ratio $I_{\|}/I_{\perp}$ of the intensities measured with a polarizer parallel and perpendicular to the preferred axis, respectively. To date, dichroic ratios larger than 20 have been achieved [13, 14]. To a less extent, preferential circular polarization of the emitted light can be achieved in suitable systems [7, 20–22].

Recently, increasing interest in the semiconducting properties of columnar liquid crystals has inspired efforts to induce a uniform alignment of these highly viscous materials. Ohta *et al.* have synthesized compounds which spontaneously form a perfect homeotropic alignment in a certain mesophase [23]. In this case, the molecules align flat on the surface so that the director (the direction of the columns) is perpendicular to the substrate. The friction deposition of poly(tetrafluoroethylene) [24–28] was successfully applied by van de Craats *et al.* [29] and Zimmermann *et al.* [30] to achieve a uniaxial alignment of the columns parallel to the plane of the substrate. As a consequence, linearly polarized absorption and photoluminescence were observed with dichroic ratios $I_{\|}/I_{\perp}$ of 6.5 and 3, respectively. Here, we report the application of the same technique to achieve polarized electroluminescence. To date, the dichroic ratio obtained is much lower than those of the electroluminescence achieved using calamitic liquid crystals. However, the effect is very clear and encouraging for future work in this direction.

2. Experimental

The synthesis of the mesogenic compound tetraethyl perylene-3,4,9,10-tetracarboxylate and its mesomorphic

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behaviour have been described previously [9]. This mesogenic compound shows a columnar mesophase at elevated temperature, and a crystalline state with columnar ordering at room temperature. For the preparation of the OLEDs, we used conventional ITO substrates. The PTFE orientation film was applied on the ITO layer by a home made apparatus, figure 1 (*a*), which follows the friction method published by Smith *et al.* [24, 25]. A cylindrical PTFE bar is pressed on the ITO-coated glass substrate while the latter is moved, continuously. Both the substrate and the PTFE bar are heated to the same temperature in the range 150–275°C. For the electroluminescent samples, PTFE films were deposited at three different temperatures (150, 200 and 250°C). We chose a velocity of $1\,\mathrm{mm\,s^{-1}}$. The PTFE rod was pressed on the substrate by a weight of 2.5 kg in all cases. After deposition of the alignment layer, the tetraethyl perylene-3,4,9,10-tetracarboxylate emitting layer was thermally evaporated (55 nm) under high vacuum (10^{-5} mbar). An aluminium layer of 100 nm thickness was evaporated as cathode on top of the organic layer, figure 1 (*b*). The samples for photoluminescence investigations were prepared in the same way, using a glass substrate without ITO and omitting the aluminium layer. A wavelength of 390 nm was used for exciting the photoluminescence. Both the polarized photoluminescence and electroluminescence spectra were measured by means of a fluorescence spectrometer (PTI, model Quanta Master QM 2000-4) equipped with a quartz polarizer as analyser. All measurements were performed at room temperature.

3. Results and discussion

The investigation of the dichroism of photoluminescence confirms that PTFE layers deposited by the friction method are quite suitable for aligning both calamitic and discotic liquid crystals. As expected, the emitted light of a calamitic nematic liquid crystal is predominantly polarized along the rubbing direction, figure 2 (*a*), while the light emitted by a columnar liquid crystal is polarized along the plane perpendicular to the rubbing direction of the PTFE layer, figure 2 (*b*). In the calamitic system, the preferred axis of uniaxial alignment corresponds to the average orientation of the molecular long axes. We used a mixture of 4-(4-pentylcyclohexyl)benzonitrile, PCH5, (which shows no fluorescence) and *N*,*N*-dimethyl-4′-nitro-4-stilbenamine, DANS, where the transition dipole moment is oriented approximately along the long axis of the molecule. The dichroic ratio obtained by a layer of several μm thickness on a PTFE alignment layer is approximately 4.1 at $\lambda = 591$ nm. The plane of polarization of the emitted light indicates that the director of the liquid crystal is aligned along the preferred axis of the alignment layer.

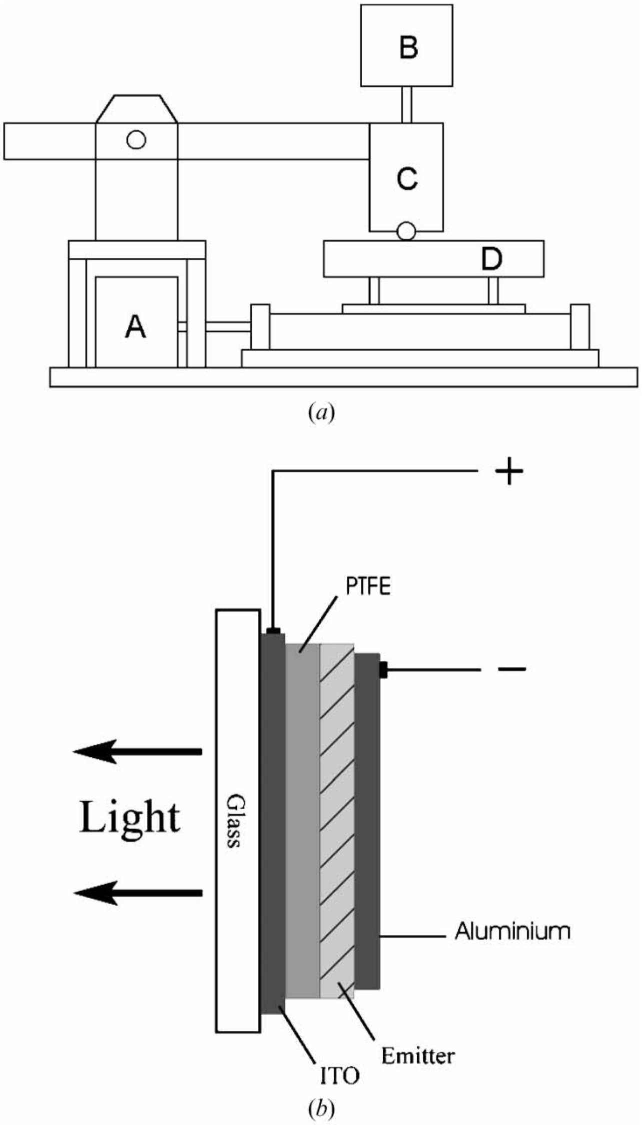
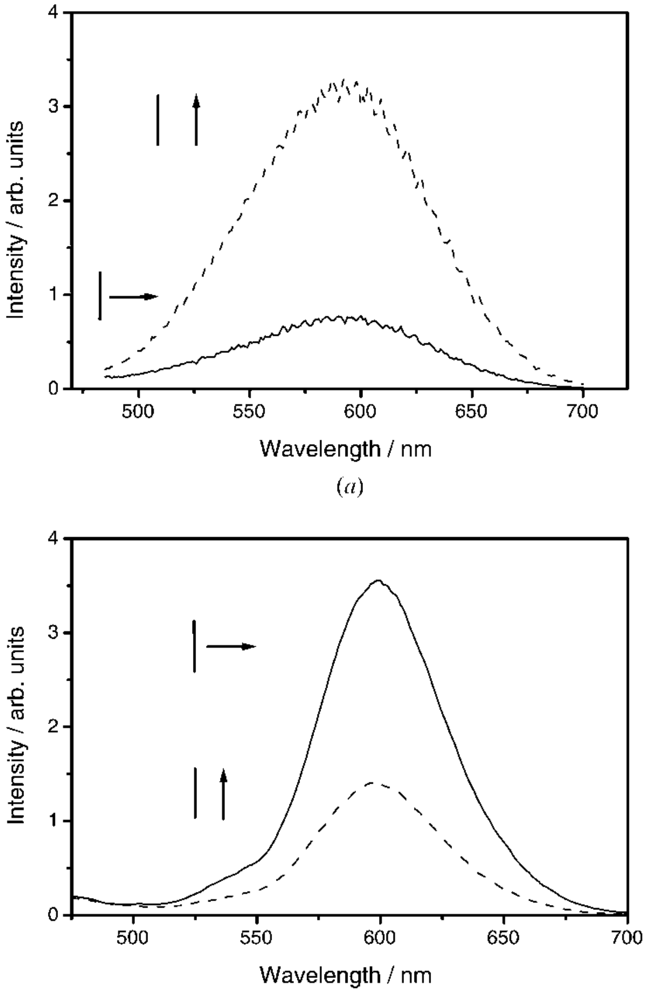


Figure 1. (*a*) Set-up for PTFE deposition. A: stepping motor, B: weight, C: temperature-controlled mount of the PTFE bar, D: moving heating stage for the substrate. (*b*) Layer sequence of the electroluminescent samples.

In contrast, the transition dipole moment of the discotic liquid crystal is in the plane of the conjugated molecule. The director of a discotic liquid crystal corresponds to the axis perpendicular to the plane of the disk-shaped molecules. Thus the average transition dipole moment is perpendicular to the director. Our observation of the dichroism of the columnar phase indicates that the director, and thus the columns, are aligned along the preferred axis of the PTFE alignment layer. Using a PTFE layer deposited at 275°C, the dichroic ratio of a thin (30 nm) layer of tetraethyl perylene-3,4,9,10-tetracarboxylate was found to be 2.5.

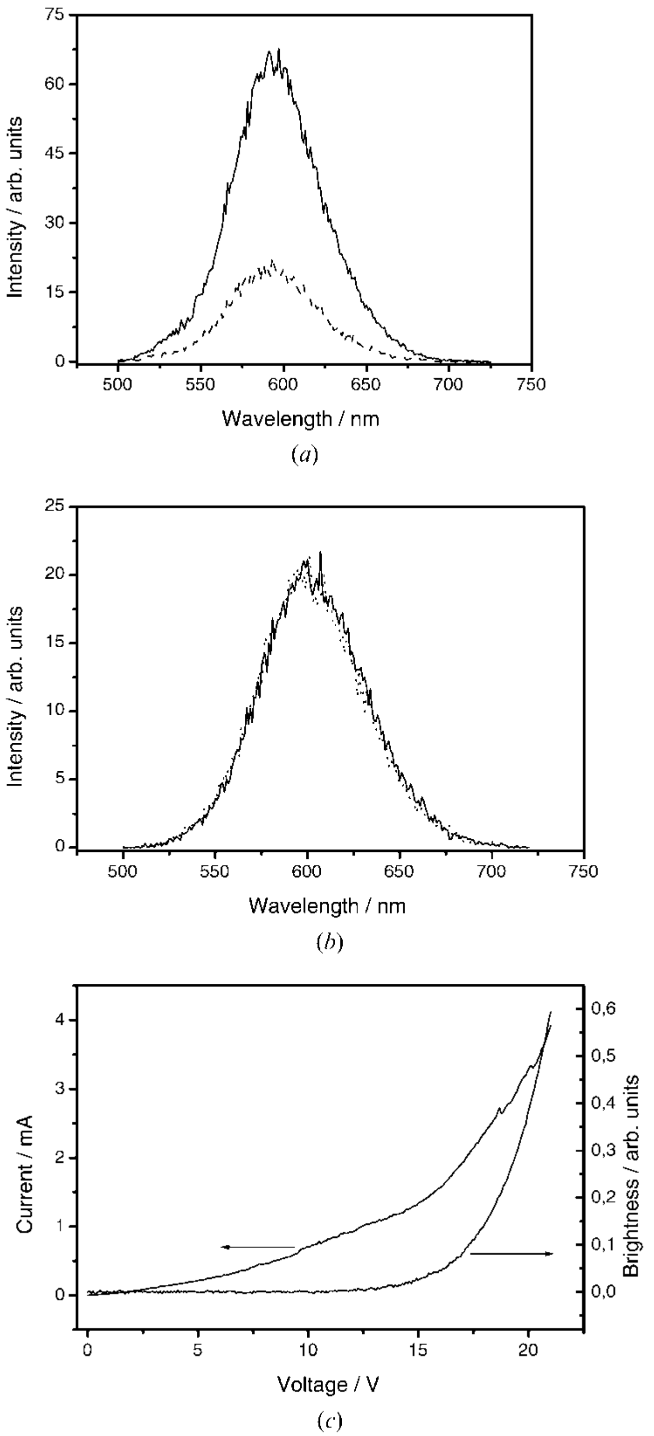


(*a*)

(*b*)

Figure 2. Dichroism of the photoluminescence; spectral distribution of the light intensity emitted perpendicular to the cell surface for different states of polarization. The insets indicate the relative orientation of the rubbing direction (bar) and the polarization (arrow = electric field direction) of the light transmitted through the analyser. (*a*) Calamitic liquid crystal mixture of *N,N*-dimethyl-4′-nitro-4-stilbenamine (≈0.11%) and 4-(4-pentylcyclohexyl) benzonitrile. (*b*) Columnar liquid crystal tetraethyl perylene-3,4,9,10-tetracarboxylate.

The electroluminescence of aligned layers was investigated in samples consisting of several thin layers which were prepared as described in § 2, figure 1 (*b*). The samples under investigation show an orange luminescence if sufficiently high d. c. voltages are applied. The use of a linear polarizer indicates that the emitted light is polarized if the sample contains an alignment layer. We measured a dichroic ratio of $I_{\parallel}/I_{\perp} = 3.2$ with a PTFE layer deposited at 200°C and a speed of $0.1\,\mathrm{cm\,s^{-1}}$, figure 3 (*a*). For comparison, figure 3 (*b*) shows the emission spectra of a sample with the same thickness



(*a*)

(*b*)

(*c*)

Figure 3. (*a*,*b*) Electroluminescence spectra, measured using a linear analyser; solid lines indicate plane of polarization horizontal, dotted lines indicate plane of polarization vertical. (*a*) Sample with PTFE alignment layer, deposited at 200°C; (*b*) sample without PTFE layer. (*c*) Current and luminescence intensity versus voltage for the sample with layer sequence ITO/PTFE/tetraethyl perylene-3,4,9,10-tetracarboxylate (55 nm)/Al.

of the mesogenic material, but without the alignment layer. In the latter case, the emitted light is unpolarized. Varying the parameters of the PTFE deposition, we found that the temperature of the preparation affects the dichroic ratio. With the same sample geometry as represented in figure 1 (*b*), deposition temperatures of 150 and 250°C result in a dichroic ratio of only 2.4 and 2.6, respectively.

The current–voltage characteristic of the sample with a relatively high dichroic ratio is presented in figure 3 (*c*). The sample shows the typical diode characteristics with a critical voltage of about 17 V. It is interesting to note that the current rises considerably even below the threshold voltage of the light emission. The other samples investigated exhibit qualitatively the same behaviour, some even showing two distinct steps of the current. The luminescence starts only at the higher threshold. We cannot fully explain the appearance of two critical voltages, but it is obvious that a mechanism of charge transport without radiation exists which competes with the electroluminescence. Of course, voltages above 18 V are not acceptable for practical applications and thus, the layer sequence of the samples has to be optimized. On the other hand, a sample exhibiting only the perylene compound and no PTFE layer shows a similar critical voltage. We conclude that the presence of the very thin PTFE layer is not the critical parameter which causes the high threshold.

In conclusion, we have found that, in principle, columnar mesogenic compounds can give polarized electroluminescence. After the observation of polarized electroluminescence from calamitic compounds and aligned polymers [11–20], and of polarized photoluminescence of columnar liquid crystals [30], this is a further step showing the potential use of mesogenic materials. Further systematic studies are now necessary to improve the dichroic ratio, to reduce the threshold voltages and to increase the efficiency of these systems.

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