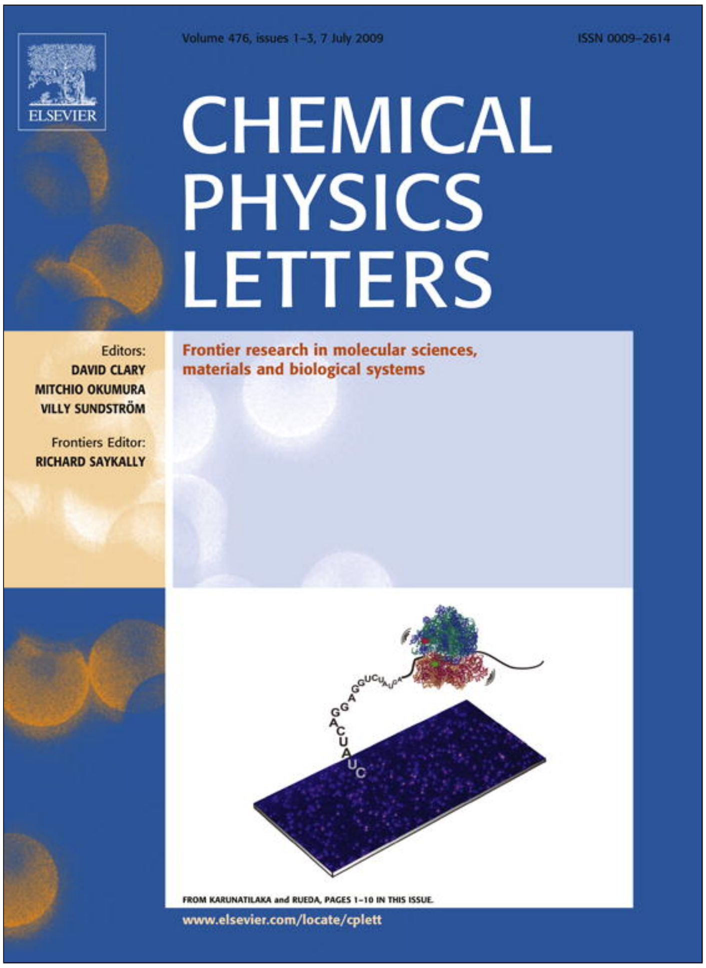
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Measurement of the exciton diffusion length in discotic columnar liquid crystals: Comparison between homeotropically oriented and non-oriented samples

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ABSTRACT

This Letter reports the determination of the singlet exciton diffusion length (L_D) for a thermotropic discotic columnar liquid crystal (CLC) in both non-oriented and homeotropically oriented (columns perpendicular to the substrate) samples. Experimental results based on photoluminescence measurements indicate that L_D is only slightly dependent on the liquid crystal orientation. Conversely, studies of ITO/CLC (50 nm)/Al Schottky-type devices formed by non-oriented and oriented liquid–crystalline films show an increase in the photocurrent by a factor of 16, due to the homeotropic alignment. This improvement is attributed to both increased light absorption and charge-carrier mobility.

1. Introduction

Organic photovoltaic cells are gaining an ever increasing interest in scientific research and energy production due to their potential of low cost fabrication onto lightweight and flexible substrates. Recent studies have led to improvements in power conversion efficiency (η_p) with values exceeding 6.5% [1]. This should be compared with the early organic photovoltaic cells reported by Tang in 1985, with a η_p slightly below 1% [2]. Despite this significant progress, an increase of η_p is still needed for practical device applications. A primary reason for the low η_p value derives from intrinsic properties of amorphous organic semiconductors, namely low exciton diffusion length (L_D) and charge-carrier mobility (μ). Although L_D and μ both depend on many factors (microscopic defects, impurities, interface traps...), a way to improve them is to increase the molecular ordering [3]. Columnar liquid crystals (CLC) are attractive materials since their mesophases permit the self-organization of disk-shaped molecules in columns. Due to the π-orbital overlap between stacked molecules, high values of L_D and μ are expected in the column direction, whereas low values are expected perpendicular to the column direction due to the insulating alkyl chain periphery of the columns. The increase in μ with the homeotropic alignment (axis of the columns perpendicular to the substrate, see Fig. 1) has been proven experimentally [4]. A correlation between L_D and μ has been reported [5,6]; however, to our knowledge, no experimental investigation has so far been performed to probe the influence of the CLC alignment on the exciton diffusion length, L_D. Recently, we have reported the achievement of very thin uniform films of homeotropically oriented thermotropic CLC (with thicknesses down to 50 nm) on an indium tin oxide (ITO)-coated glass substrate [7]. Taking advantage of the control of liquid crystal alignment in the geometry of thin films, we focus in this work on determining the exciton diffusion length L_D in both non-oriented and homeotropically oriented columnar liquid crystal films and on characterizing the photocurrent in the organic photovoltaic devices based on these films.

2. Experimental

The chemical structure of the CLC used, benzo[g,h,i]perylene 1,2,4,5,10,11-hexacarboxylic 1,2-di-(2-ethylhexyl)ester 4:5,10:11-di-(4-heptyl)imide, is shown in Fig. 1. This discotic material exhibits a hexagonal CLC phase at room temperature [8]. Glass substrates were used for L_D measurements. They were first cleaned with two successive ultrasonic baths of acetone and ethanol (15 min each), and rinsed with deionised water. They were then dried under dry nitrogen before an atmospheric pressure plasma treatment in pure nitrogen during 2 min [9]. The pressure during the evaporation of the discotic compound was 1×10^{-4} Pa and the deposition rate was kept constant at 0.1 nm s^{-1}. One set of CLC films was homeotropically oriented onto the treated glass substrate following the thermal process described in Refs. [7,10], while another one was kept non-oriented i.e. exhibiting a degenerated planar alignment [8,10]. All the samples were covered with a thin layer (10 nm thick) of an exciton quencher spread over one half of the film surface. The choice of zinc phthalocyanine (ZnPc) as exciton quencher was based on measurement of electronic affinity

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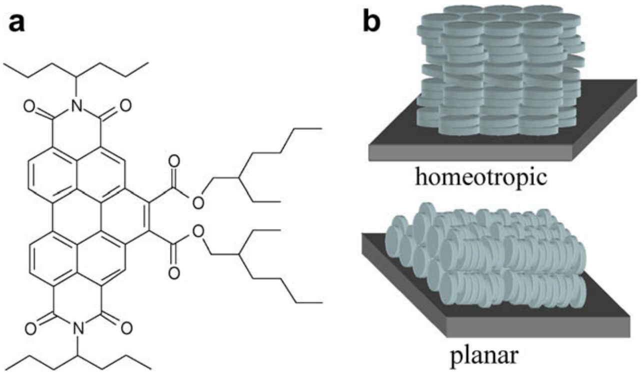

Fig. 1. (a) Molecular structure of the benzoperylene derivative used. This compound exhibits a hexagonal columnar phase from $T_{\text{CLC-iso}} = 225\,°\text{C}$ to ambient temperature. (b) Representation of the homeotropic and planar orientations of a columnar mesophase.

(3.7 eV) of the discotic compound by cyclic voltammetry. The average value (5 eV) of ZnPc ionization potential found in literature allowed us to establish that dissociation of excitons with an energy higher that 5–3.7 = 1.3 eV should occur by electron transfer at the CLC/ZnPc interface. This condition is verified for the studied material with an optical energy gap of 2.5 eV obtained from absorption spectrum. However, due to an existing overlap of the photoluminescence spectrum of CLC and the absorption spectrum of ZnPc, energy transfer from CLC to the quencher may also occur. The low ZnPc film thickness allowed us to check by optical microscopy that the homeotropic orientation of the columnar liquid crystal was preserved after the deposition of the quencher. The thicknesses of the organic films were controlled in situ by a quartz microbalance and confirmed by mechanical profilometer measurements. Photoluminescence (PL) spectroscopy (Xenius Spectrofluorometer, SAFAS) was used to investigate the singlet exciton diffusion length, L_D, of the columnar liquid crystal. The experimental method consisted in the measurement of the steady-state PL on a heterostructure as described in Fig. 2, and monitoring the fluorescence intensity as a function of the thickness of the CLC layer [11]. The latter was excited through the glass side at a wavelength of 444 nm, corresponding to the maximal absorption of the material. The PL intensity was measured at 555 nm corresponding to the maximum in the luminescence spectrum. For different thicknesses of the organic layer, measurements were taken in both parts of CLC layer: the one covered with the ZnPc (PL1 intensity) and the other uncovered surface (PL2 intensity).

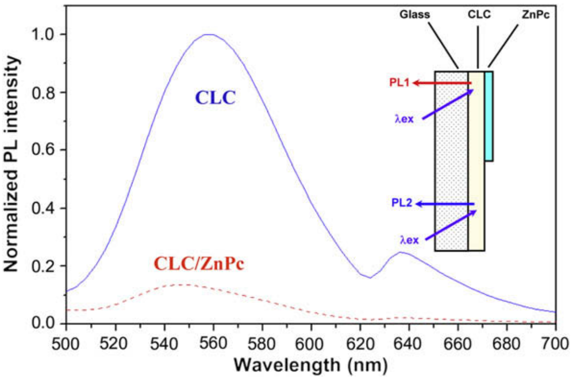

Fig. 2. The schematic representation of the experimental geometry is given on the right side. Light was incident on the glass/CLC interface. Some fraction of the excitons passes through the CLC film of thickness *d* and reaches the ZnPc layer where the excitons can be quenched. The PL spectra of a 20 nm thick CLC film with a 10 nm thick ZnPc layer on top (dashed line) is lower than the PL of a film without the ZnPc layer (continuous line).

Both non-oriented and homeotropically aligned sandwich-type cells of ITO/CLC/Al were also fabricated with a 50 nm thick CLC layer for determining their short-circuit photocurrent density, J_{sc}. The ITO was purchased from VisionTek Systems Ltd. (sheet resistance of 15 Ω/sq., thickness of 150 nm). They were cleaned and treated with the atmospheric pressure plasma method as described above, to prevent the instability of the CLC film in the isotropic liquid phase during the thermal annealing [7]. To compare experimental results, the same treatment was applied to all the ITO electrodes although it was not necessary for non-oriented CLC components. Indeed, the work function of the ITO can be affected by the surface treatments which in turn lead to the modification of solar cell characteristics [12]. An aluminium electrode (100 nm thick) was evaporated at $1\ \text{nm}\ \text{s}^{-1}$ onto CLC films. The photoactive area was $10\ \text{mm}^2$ and the photocurrent was measured by illuminating the samples with a xenon lamp.

3. Results and discussion

In a first approximation, by considering a sharp exciton dissociation interface, the exciton diffusion length can be directly determined from steady-state quenching of the time-integrated photoluminescence [13]. The relative quenching ratio PL1/PL2 is then given by:

$$\frac{\text{PL1}}{\text{PL2}} = 1 - \frac{[\alpha^2 L_D^2 + \alpha L_D \tanh(d/L_D)]\exp(-\alpha d) - \alpha^2 L_D^2 \cosh(d/L_D)^{-1}}{(1-\alpha^2 L_D^2)[1-\exp(-\alpha d)]} \tag{1}$$

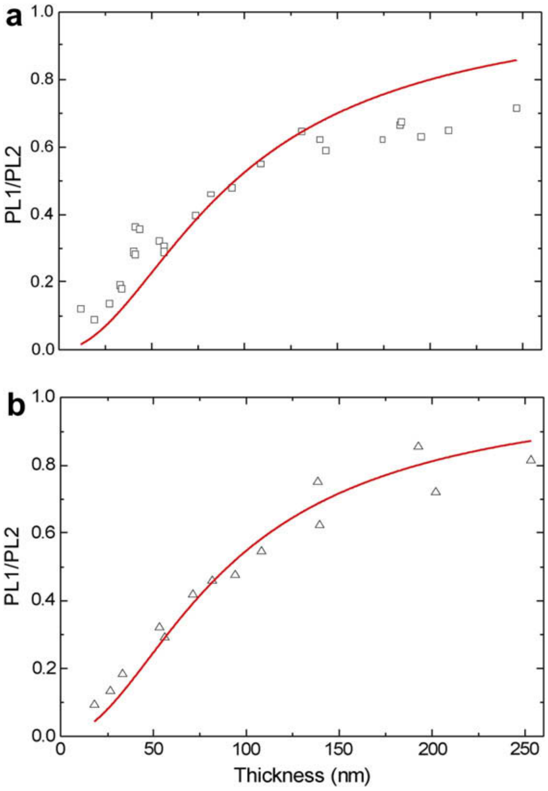

Fig. 3. Relative quenching ratio PL1/PL2 as a function of the non-oriented CLC film thickness (a) for glass/CLC/ZnPc samples, (b) for inverted structures: glass/ZnPc/CLC. The red full lines are a data fit according to Eq. (1) giving $L_D = 52 \pm 4$ nm and 50 ± 2 nm for glass/CLC/ZnPc and glass/ZnPc/CLC samples, respectively.

where d is the CLC film thickness and α is the light absorption coefficient [11]. The value of α has been shown to depend on the liquid crystal orientation, with $\alpha = 8.9 \times 10^{-3}$ nm^{-1} and 5.2×10^{-3} nm^{-1} at 444 nm for the homeotropically aligned and the non-oriented samples, respectively [8]. Due to the thin quencher layer, interference effects are neglected. To exclude the possibility of imperfect quenching at the ZnPc interface, the PL of a 20 nm CLC film topped by a 10 nm ZnPc quencher layer was monitored. As expected, the PL intensity of half of the CLC film covered with the quencher was greatly reduced, by more than 85%.

For non-oriented CLC films, the best fit of the experimental data using Eq. (1) with the exciton diffusion length L_D as a free parameter yields $L_D = 52 \pm 4$ nm (Fig. 3a). During the quencher evaporation process, some ZnPc molecules may diffuse into the CLC film: the distance an exciton has to travel would thus be lower than the predicted value. To study this possibility, which would lead to an overestimation of the L_D value [14], we performed the same measurements in a reversed structure with 10 nm ZnPc evaporated at first on the glass substrate, then covered with the CLC film. For these samples, the best data fit is obtained for $L_D = 50 \pm 2$ nm (see Fig. 3b), showing that the diffusion of organic compounds in each other is negligible with respect to the precision of the measurement. For homeotropically oriented CLC layers, an exciton diffusion length of $L_D = 62 \pm 2$ nm (Fig. 4) is found according to Eq. (1). The values of L_D obtained for oriented and non-oriented layers are probably overestimated due to energy transfer between CLC and ZnPc, which implies that excitons do not have to reach the interface to undergo dissociation. However, this phenomenon should be slightly dependent on the film orientation; the enhancement of about 20% of L_D between homeotropically aligned and non-aligned CLC samples is lower than what we initially expected. Therefore, long-range dipolar interactions are likely to be the predominant singlet energy transfer mechanisms as well in oriented or non-oriented layers, as quantified theoretically in a triphenylene columnar liquid crystal by Markovitsi et al. [15].

Despite this result, the importance to have the CLC in homeotropic orientation is shown here by photocurrent measurement. When ITO/CLC/Al sandwich-type devices are irradiated from the transparent ITO side, the short-circuit photocurrent density (J_{sc}) can be determined: the action spectrum follows the absorption spectrum of the CLC film. The experimental results indicate that a maximum J_{sc} of 0.07 μA cm^{-2} is obtained for non-oriented CLC devices (Fig. 5). For a homeotropically oriented CLC sample, the maximum of J_{sc} is 1.12 μA cm^{-2}. This huge enhancement in J_{sc} is mainly attributed to both increased light absorption and charge mobility, in the absence of data concerning triplet exciton diffusion length in our systems.

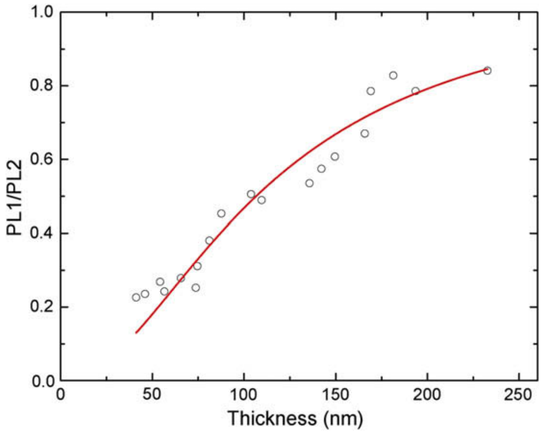

Fig. 4. Relative quenching ratio PL1/PL2 of glass/CLC/ZnPc samples versus film thickness for homeotropically aligned CLC layers. An exciton diffusion length of 62 ± 2 nm is found using Eq. (1) for the data fit.

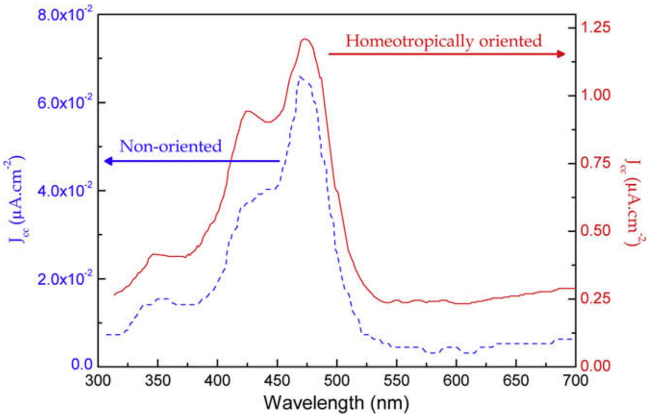

Fig. 5. Photocurrent action spectra of ITO/homeotropically oriented CLC (50 nm)/Al (solid line) and ITO/non-oriented CLC (50 nm)/Al cells (dashed line).

In conclusion, we have shown in this work a slight enhancement of the singlet exciton diffusion length of columnar liquid crystals with the homeotropic orientation. Conversely, the study of ITO/CLC (50 nm)/Al Schottky-type devices based on oriented and non-oriented CLC films exhibits an increase in the short-circuit photocurrent by a factor of 16 due to the film orientation. Our results suggest that the singlet exciton migration is mainly *isotropic*, contrary to charge migration which is shown to be strongly *anisotropic*. This dependence of optoelectronic behavior on the liquid crystal orientation should stimulate further theoretical and experimental investigations.

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