# The effect of chiral liquid crystalline compound on P3HT:C60 bilayer solar cells

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We have investigated the effect of chiral (S)-5-octyloxy-2-[{4-(2-methylbuthoxy)-phenylimino}-methyl]phenol Liquid Crystalline Compound (LCC) addition into P3HT:C60 solar cells. Based on current-voltage characteristics, the efficiency of devices with liquid crystal is found to be higher than that of devices from pristine blends of P3HT:C60. Significant improvements have been achieved by using this liquid crystal additive.

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## 1. Introduction

Photovoltaic devices based on organic materials have attracted attention in the last years because of their advantageous properties, such as low cost, light weight, possibility of producing large area and flexible devices [1–7]. The main focus in the organic solar cell research lies on increasing the power conversion efficiency [6–8]. Several approaches for efficiency improvement have been proposed, especially regarding geometry and materials synthesis. Nowadays several research groups have reported power conversion efficiencies around 10% (Mitsubishi Chemicals, Konarka and Heliatek, [9–11]) motivating even more the research in the field.

Poly(3-hexylthiophene) (P3HT) has attracted a lot of attention as a donor material, as it has one of the highest charge carrier mobility among the conjugated polymers with a hole mobility exceeding 0.1 $cm^2/Vs$ and an absorption edge around 650 nm [12]. These qualities make P3HT a good candidate in polymer photovoltaic cells [8, 13, 14].

The use of a C60 molecule (that has high electroaffinity value) sublimed onto the polymer in a heterojunction (bi-layer) or mixed in the polymer film (bulk heterojunction blend) increased drastically the efficiency of the photovoltaic devices [15–17]. Bilayers devices can be quite efficient in photoconversion if the thickness of the layers are within the exciton diffusion length, with the exciton dissociation occuring at the interface of the photoactive materials due to the difference of the electronaffinity values.

Schmidt-Mende and co-workers reported a novel methodology of controlling nanostructured p-n junction in OPVs using discotic liquid crystal molecules and they have reported that using liquid crystal molecules, charge transport in OPVs could be enhanced [18, 19]. Furthermore, effects of a chemical additive into polymer/fullerene bulk-heterojunctions have been investigated by several groups. Using chemical additives results in significant improvement of the efficiency of organic solar cells and it is rather simple method as compared to other treatments [20-21].

Liquid crystals have tremendous success in commercial applications [22–26]. They are very sensitive to external fields [27]. Liquid crystal displays are inexpensive and work under low operational voltage and low power consumption: such displays can also often operate in the presence of sunlight (because they modulate the reflected light including the sunlight itself and thus maintain a good contrast).

We have reported this chiral smectic liquid crystal additive into P3HT:PCBM based bulk heterojunction solar cells [28]. In this paper, we report on properties of organic solar cells fabricated from P3HT:C60 bilayer by adding this liquid crystal (LCC).

Among the materials showing liquid crystal phases, salicyaldimine compound liquid crystal materials are rather new and interesting family with their specific structures. Especially for the OPV applications, structure of liquid crystals could play an important role. In order to optimize the performance of organic solar cells fabricated from polymer/fullerene mixtures with liquid crystal it is necessary to understand the influence of the additive to the molecular rearrangement as well as to the optical, photo physical and electrical properties of the blends.

A significant increase in power conversion efficiency is seen in the bilayer solar cells with LCC as additive.

## 2. Experimental

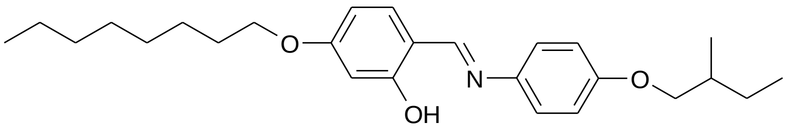
### 2.1 Material

The preparation procedure and spectroscopic dates for (S)-5-octyloxy-2-[{4-(2-methylbuthoxy)-phenylimino}-methyl]phenol (LCC) is given by us in [29]. The liquid crystalline properties, dielectric dynamics and dielectric anisotropy properties of the chiral salicylaldimine compound (LCC) synthesized by our group, have been investigated in detail and reported in [29-32].

The mesomorphic properties of the salicylaldimine compound (LCC) have been studied by polarizing microscopy (PM) technique using a Linkam THMS 600 hot stage and a Linkam TMS 93 temperature control unit in conjunction with a Leitz Laborlux 12 Pol polarizing microscope, and these were confirmed using differential scanning calorimetry (DSC). The compound LCC has prolate molecules and exhibits the chiral smectic C* mesophase in a sufficiently large temperature interval (Fig. 1a) [31].

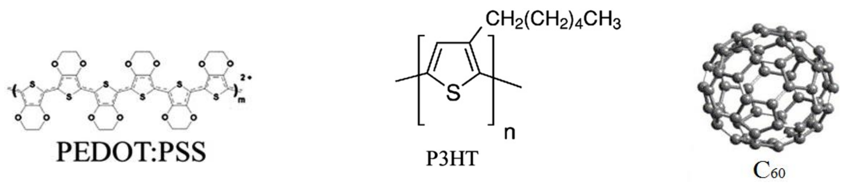
**2.2 Solar cell preparation**

The polymer based organic solar cells in this study consist of P3HT:C60 bilayer structure with and without LCC. The photo active layer is deposited by spin coating on the indium tin oxide (ITO) glass substrates with a sheet resistance of 30 $\Omega cm^{-2}$. The ITO was patterned by etching with an acid mixture ($HCl:HNO_3:H_2O$=4.6:0.4:5) for 40 min. The part of the substrate which forms the contact was covered with a scotch tape in order to prevent the etching. The scotch tape was removed after etching and the substrate was then cleaned by using acetone in an ultrasonic bath and finally with iso-propanol. An aqueous solution of poly(3,4-ethylenedioxythiophene)–poly(styrenesulfonate) (PEDOT:PSS) (Fig. 1b) was spin cast on the glass–ITO substrate to facilite charge injection and extraction. Then annealed 140$^{o}$C 5 min. then dried under a dynamic vacuum.




(a)

Cr *31.2 (24.8)* SmC* *84.3 (11.4)* Iso




(b)

*Fig. 1. (a) The chemical structure and phase transition temperatures T (°C) and transition enthalpies $\Delta H$ (kJ mol$^{-1}$) of the LCC (Perkin-Elmer DSC-7; heating rates 10 K min$^{-1}$ for the melting and clearing process. Cr: crystalline, SmC*: chiral smectic and Iso: isotropic phase). (b) Chemical structures of PEDOT: PSS, P3HT and C60.*

All polymers, P3HT and LCC mixed solutions were stirred for 24 h before spin coating to ensure that the P3HT and LCC have been completely dissolved in solution.

The device structure and configuration of cells are shown in Fig. 3 P3HT and P3HT: LCC in clorobenzene was spin-coated on the PEDOT: PSS layer. In this report, the amount of LCC was 1 mg while structure of P3HT: LCC = 5:1 (5 mg/1 mg ratio) was kept constant. C60 (60 nm) was evaporated in vacuum. Al (~150 nm) metal was used as a top electrode.

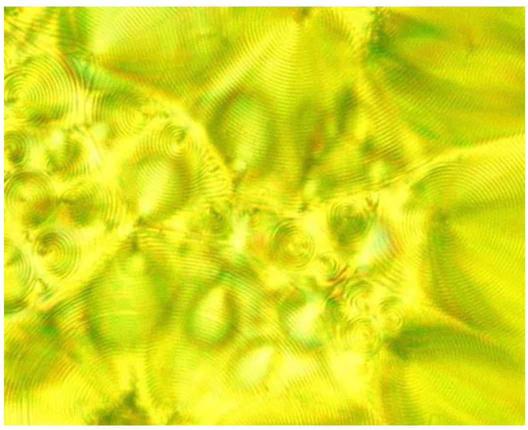


*Fig. 2. Polarized light optical photomicrograph of the LCC.*

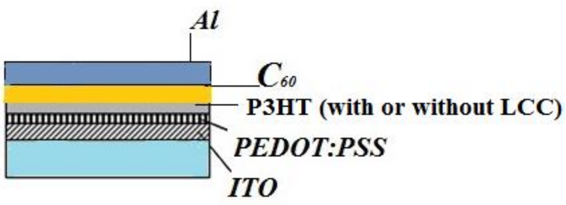



*Fig. 3. The device structure of cells.*

### 2.3 Current-Voltage, IPCE and absorption characteristics

All current–voltage (I–V) characteristics of the PV devices were measured (using a Keithley SMU 236) under nitrogen in a dry glove box immediately after production. A Steuernagel solar simulator, simulating AM1.5 conditions, was used as the excitation source with an input power of 100 mW/cm$^2$ white-light illumination.

The spectrally resolved photocurrent was measured with an EG&G Instruments 7260 lock-in amplifier. The samples were illuminated with monochromatic light from a Xenon lamp. The incident photon to current efficiency (% IPCE) was calculated according to the following equation:

$$\text{IPCE}\ (\%) = \frac{I_{sc} * 1240}{P_{in} * \lambda_{incident}}$$

Where $I_{sc}$ ($\mu$A/cm$^2$) is the measured current under short-circuit conditions of the solar cell, $P_{in}$ (W/m$^2$) is the incident light power, measured with a calibrated silicon diode, and $\lambda$ (nm) is the incident photon wavelength.

The optical absorption spectrum was investigated by means of UV-VIS Varian Carry 3G UV-Visible spectrophotometer spectroscopy.

## 3. Results and discussions

### 3.1 Photovoltaic properties of P3HT:C60 and P3HT:LCC:C60 devices

Current density-voltage (J-V) characteristics for all cells with and without LCC under illumination are shown in Fig. 4. The device parameters of untreated devices with and without LCC (short-circuit current density ($J_{sc}$), open circuit voltage ($V_{oc}$), fill factor (FF), for these cells are summarized in Table 1. The performance of untreated device without LCC was rather poor. Untreated solar cells without LCC have the worst performance with the lowest short-circuit current density (0.57 mA/cm$^2$) and low fill factor (0.358). However, these cells demonstrate a relatively low open-circuit voltage (200 mV) but due to the low short-circuit current and the low fill factors; their power conversion efficiency was found to be around % 0.04.

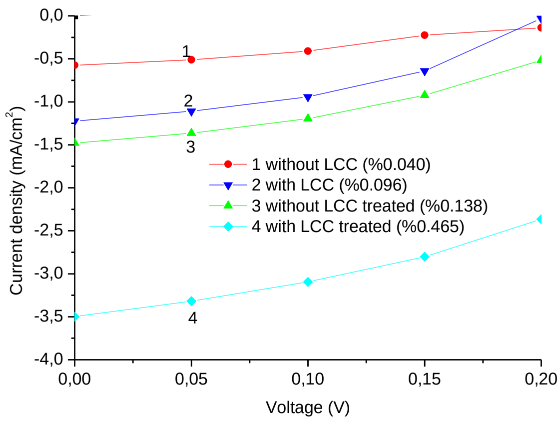



*Fig. 4. Current density voltage curves in the four different P3HT:C60 bilayer solar cells under illumination with solar simulator (100 mW/cm$^2$, AM 1.5): as produced, annealed (T=150$^o$C, 30 min), 1 mg LCC added and annealed film.*

*Table 1. Photovoltaic parameters for the treated and untreated devices with (1 mg) and without LCC (T=150 $^o$C, t=30 min.).*

| | FF | Voc (mV) | Jsc (mA/cm$^2$) | η(%) |
|---|---|---|---|---|
| untreated without **LCC** | 0.358 | 200 | 0.57 | 0.040 |
| treated without **LCC** | 0.375 | 250 | 1.48 | 0.138 |
| untreated with **LCC** | 0.393 | 200 | 1.22 | 0.096 |
| treated with **LCC** | 0.380 | 350 | 3.5 | 0.465 |

The effect of annealing, to the photovoltaic performance of P3HT:C60 and P3HT: LCC:C60 devices was also investigated. The annealing temperatures for were set as 150 $^o$C and 100 $^o$C for 30 min. After annealing at 150 $^o$C for 30 min, significant improvement in photovoltaic performance was observed (Table 1).

Comparing the J-V curves of treated devices, with that of the untreated device, a distinct difference was in the increase of $J_{sc}$, FF and the efficiency. The device parameters for these cells summarized in Table 1 and Table 2. These photovoltaic parameters were considerably improved with annealing. As shown in Fig. 4 and Table 1, Table 2, all photovoltaic performance parameters are improved when P3HT is mixed with LCC. We have measured the incident photon to current efficiency (IPCE) in all four types of cells and results are shown in Fig. 5. After annealing, the overall efficiency (IPCE) was increased six fold as compared to that of the untreated device.

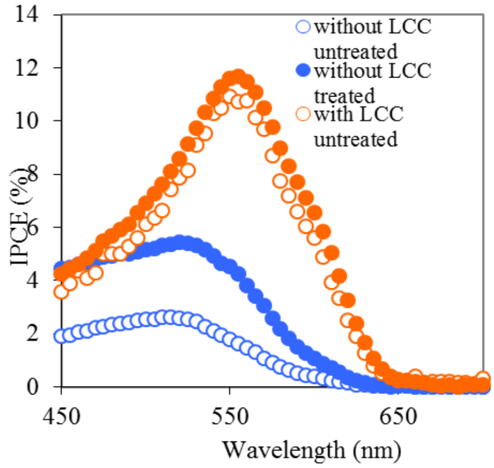



*Fig. 5. Incident photon to current efficiency of P3HT:C60 bilayer solar cells: as produced, annealed, LCC added, LCC added and annealed film.*

*Table 2. Photovoltaic parameters for the treated and untreated devices with (1 mg) and without LCC (T=100 °C, t=30 min).*

| | FF | Voc (mV) | Jsc (mA/cm$^2$) | η(%) |
|---|---|---|---|---|
| untreated without **LCC** | 0.337 | 150 | 1.42 | 0.071 |
| treated without **LCC** | 0.428 | 150 | 1.58 | 0.101 |
| untreated with **LCC** | 0.317 | 200 | 2.4 | 0.152 |
| treated with **LCC** | 0.359 | 200 | 2.73 | 0.196 |

## 4. Conclusions

Normally P3HT:C60 bilayer heterojunction solar cells have low photovoltaic performance. There can be two ways to approach to improve the low performance of bilayer P3HT and C60 bilayer heterojunction solar cells: either to focus within the layer stack itself or to find other alternative ways such as addition of materials which could improve the morphology, e.g. as in this study addition of a liquid crystal. We have earlier reported the investigation of the effect of LCC addition into bulk-heterojunction solar cells, based on P3HT and PCBM mixtures. We have found very interesting results such as improvement in charge carrier mobility/extraction and efficiencies in the P3HT: PCBM blends with the liquid crystal LCC [28].

In this study we have studied the role of liquid crystal addition in P3HT:C60 bilayer solar cells. The effect of LCC in P3HT:C60 solar cells was the increase in short circuit current density from 0.57 mA/cm$^2$ to 3.5 mA/cm$^2$ and result in substantial improvement of power conversion efficiency from 0.04 % to 0.46 % P3HT:LCC:C60 solar cell with an optimized amount of liquid crystal (1mg).

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## References

[1] C. J. Brabec, N. S. Sariciftci, J. C. Hummelen, Plastic Solar cells, Adv. Funct. Mater. **11**, 15 (2001).
[2] H. Spanggaard, F. C. Krebs, Sol. Energy Mater. Sol. Cells **83**, 125 (2004).
[3] C. Winder, N. S. Sariciftci, J. Mater. Chem. **14**, 1077 (2004).
[4] E. Bundgaard, F. C. Krebs, Sol. Energy Mater. Sol. Cells **91**, 954 (2007).
[5] F. C. Krebs, J. Alstrup, H. Spanggaard, K. Larsen, E. Kold, Sol. Energy Mater. Sol. Cells **83**, 293 (2004).
[6] S. Gunes, H. Neugebauer, N. S. Sariciftci, Chem. Rev. **107**, 1324 (2007).
[7] F. C. Krebs, H. Spanggaard, T. Kjaer, M. Biancardo,

J. Alstrup, Mater. Sci. Eng. B **138**, 106 (2007).
[8] F. Padinger, R. S. Rittberger, N. S. Sariciftci, Adv. Funct. Mater. **13**, 85 (2003).
[9]http://content.yudu.com/A1th2v/EOAUGSEP11/resources/16.htm.
[10]http://www.konarka.com/index.php/company/our-history/.
[11]http://techcrunch.com/2011/04/06/mitsubishi-chemical-to-commercialize-printablesolar-cells-next-year/.
[12] D. H. Kim, Y. D. Park, Y. S. Jang, H. C. Yang, Y. H. Kim, J. I. Han, D. G. Moon, S. J. Park, T. Y. Chang, C. W. Chang, M. K. Joo, C. Y. Ryu, K. W. Cho, Adv. Func. Mater. 15, 77 (2005).
[13] N. Camaioni, G. Ridolfi, G. C. Miceli, G. Possamai, M. Maggini, Adv. Mater. **14**, 1735 (2002).
[14] I. Riedel, V. Dyakonov, Phys. Status. Solidi. **201**, 1332 (2004).
[15] N. S. Sariciftci, L. Smilowitz, A. J. Heeger, F. Wudl, Science **258**, 1474 (1992); N. Sariciftci, A.J. Heeger, US Patent No: 5331183; N. S. Sariciftci, D. Braun, C. Zhang, V. Srdanov, A. J. Heeger, F. Wudl, Appl. Phys. Lett. **62**(6), 585 (1993); G. Yu, A. J. Heeger, J. Appl. Phys. **78**, 4510 (1995).
[16] L. S. Roman, W. Mammo, M. R. Andersson, O. Inganäs, Adv. Mater. **9**, 1164 (1997).
[17] L. S. Roman, W. Mammo, L. A. A. Pettersson, M.R. Andersson, O. Inganäs, Adv. Mater. **10**, 774 (1998).
[18] L. Schmidt-Mende, A. Fechtenkotter, K. Mullen, E. Moons, R. H. Friend, J. D. Mackenzie, Science **293**, 1199 (5532) (2001).
[19] L. Schmidt-Mende, A. Fechtenkotter, K. Mullen, R. H. Friend, J. D. Mackenzie, Phys. E. Low-Dimensional Syst. Nanostruct. (Amsterdam, Netherlands), **14**(1-2), 263 (2002).
[20] J. Peet, J. Y. Kim, N. E. Coates, W. L. Ma, D. Moses, A. J. Heeger, G. C. Bazan, Nat. Mater. **6**(7), 497 (2007).
[21] A. Pivrikas, P. Stadler, H. Neugebauer, N. S. Sariciftci, Organic Electronics **9**, 775 (2008).
[22] P. J. Collings, M. Hird, Taylor and Francis, London 1997.
[23] P. J. Collings, J. S. Patel, in 'Handbook of Liquid Crystal Research', Oxford University Press, Oxford 1997.
[24] D. Demus, J. W. Goodby, G. W. Gray, H.-W. Spiess, V. Vill, in 'Handbook of Liquid Crystals', Wiley-VCH, Chichester 1998.
[25] G. W. Gray, in 'Thermotropic Liquid Crystals', Wiley, Chichester 1987.
[26] S. M. Kelly, 'Flat Panel Displays Advanced Organic Materials', ed. J. A. Connor, Royal Society of Chemistry, Cambridge 2000.
[27] Frederics, V. K., Zolina, V. J. R. F. (Kharkov) (Phys.) **62**, 457 (1969); Tsvetkov, V. N. and Sosnovskii, A. Acta Phys. Chim. USSR 18 358 1943.
[28] N. Y. Canli, S. Günes, A. Pivrikas, A. Fuchsbauer, D. Sinwel, N. S. Sariciftci, O. Yasa, B. Bilgin-Eran, Solar Energy Materials & Solar Cells **94**, 1089 (2010).
[29] N. Yilmaz Canli, A. Nesrullajev, Ö. Yasa, B. Bilgin Eran, J. Optoelectron. Adv. Mater. 577 (2009).
[30] A. Nesrullajev, B. Bilgin-Eran, Crystal Research and Technology **43**, 308 (2008).
[31] B. Bilgin-Eran, A. Nesrullajev, N. Yilmaz Canli, Materials Chemistry and Physics, **111**, 555 (2008).
[32] N. Yilmaz Canli, Ö. Yasa, C. Yörür, B. Bilgin Eran, F. Yakuphanoglu, Optoelectron. Adv. Mater. Rapid Comm. **4**(1), 86 (2010).

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