Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Bipolar Carrier Transport in Tri-Substituted Octyloxy-Truxene DLC

H. Monobe [a], C. Chen [b], K.-Q. Zhao [b], P. Hu [b], Y. Miyake [a c], A. Fujii [c], M. Ozaki [c] & Y. Shimizu [a]

[a] Research Institute for Ubiquitous Energy Devices, National Institute of Advanced Industrial Science and Technology (AIST), Midorigaoka, Ikeda, Osaka, Japan

[b] College of Chemistry and Materials Science, Shichuan Normal University, Chengdu, Shichuan, China

[c] Graduate School of Engineering, Osaka University, Yamada-oka, Suita, Osaka, Japan

Version of record first published: 30 Jun 2011.

To cite this article: H. Monobe, C. Chen, K.-Q. Zhao, P. Hu, Y. Miyake, A. Fujii, M. Ozaki & Y. Shimizu (2011): Bipolar Carrier Transport in Tri-Substituted Octyloxy-Truxene DLC, Molecular Crystals and Liquid Crystals, 545:1, 149/[1373]-155/[1379]

To link to this article: http://dx.doi.org/10.1080/15421406.2011.568891

Mol. Cryst. Liq. Cryst., Vol. 545: pp. 149/[1373]–155/[1379], 2011

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2011.568891

Taylor & Francis
Taylor & Francis Group

Bipolar Carrier Transport in Tri-Substituted Octyloxy-Truxene DLC

H. MONOBE,[1] C. CHEN,[2] K.-Q. ZHAO,[2] P. HU,[2]
Y. MIYAKE,[1,3] A. FUJII,[3] M. OZAKI,[3] AND
Y. SHIMIZU[1]

[1]Research Institute for Ubiquitous Energy Devices, National Institute of Advanced Industrial Science and Technology (AIST), Midorigaoka, Ikeda, Osaka, Japan
[2]College of Chemistry and Materials Science, Shichuan Normal University, Chengdu, Shichuan, China
[3]Graduate School of Engineering, Osaka University, Yamada-oka, Suita, Osaka, Japan

In this study, bipolar charge carrier transport of 2,7,12-trioctyloxytruxene has been studied by a time-of-flight method. The substance studied exhibits a hexagonal columnar mesophase of which melting and clearing points are 118°C and 133°C, respectively. Ambipolar electronic carrier transports were observed in the mesophase. The drift mobility measurements reveal it is in the order of 10^{-2} cm^2 V^{-1} s^{-1} in the Col_h and it increases to 10^{-1} cm^2 V^{-1} s^{-1} at the columnar mesophase - metastable phase transition, indicating truxene is an interesting molecular core for mesophase semiconductors.

Keywords Charge carrier transport; discotic liquid crystals; mesopahse semiconductor; truxene

1. Introduction

Discotic liquid crystals (DLCs) have shown some interesting features for their electronic properties such as charge transport along the columnar axis as well as the anisotropic property of conduction in the recent decade [1–13]. In fact, in highly ordered columnar mesophases, fast carrier mobility ($\sim 10^{-1}$ cm^2 V^{-1} s^{-1}) by electronic process of charge carrier transport was found which is comparable to those of amorphous silicon [3–6]. Thus, the applications for organic semiconductors such as one-dimensional conductors, photoconductors, molecular wires and fibers, light emitting diodes and photovoltaic cells have also been exploited [14,15]. Furthermore, DLCs are expected as a self-assembling molecular semiconductor ink to fabricate the

Address correspondence to H. Monobe, Research Institute for Ubiquitous Energy Devices, National Institute of Advanced Industrial Science and Technology (AIST), Midorigaoka, Ikeda, Osaka 563-8577, Japan. Tel.: +81-72-7519149; Fax: +81-72 7519628; E-mail: monobe@ni.aist.go.jp

organic electronic devices by solution process. In particular, those are deeply interesting materials in terms of printed electronics. In addition, the ambipolar charge carrier transport is another important property as the organic semiconductors [16]. Liquid crystalline semiconductors are very effective in improving the present device with their unique features of electrically inactive structural defects including domain boundaries and fast bipolar charge carrier mobility.

Especially for discotic liquid crystalline semiconductors, molecules self-organize to molecularly stacked columnar structure and these molecular order could be active as 1D path for charge transport by electronic hopping process. Therefore, different types of π-conjugated molecular core of DLC are exploited its charge carrier mobility such as triphenylene [1–4,10–13], hexabenzocoronene [5], phthalocyanine [6], porphyrin [7], perylene [8], pyrene and carbazole [9] and those carrier mobility in the columnar mesophases are in the order of 10^{-4} to $10^{-1}\,cm^2\,V^{-1}\,s^{-1}$. On the other hand, truxene is another interesting core structure for DLCs as an organic transistor and photoconductor while those charge carrier mobility are 10^{-3} and $10^{-4}\,cm^2\,V^{-1}\,s^{-1}$, respectively [17,18]. Recently, we reported the fast hole mobility of 2,7,12-trioctyloxytruxene (in short Trx(OC8)3) by a time-of-flight (TOF) method and its hole drift mobility is around $2 \times 10^{-2}\,cm^2\,V^{-1}\,s^{-1}$ in the hexagonal columnar (Col_h) mesophase [19].

In the present report, charge carrier transport was investigated for a truxene-based DLC, Trx(OC8)3, by TOF method to show that bipolar electronic carrier transports in the mesophase. Temperature dependence of positive and negative charge carrier mobility were also reported correlated to the mesomorphism.

2. Experimental Methods

A truxene-based DLC, Trx(OC8)3, has been synthesized through six steps and synthetic routes is shown in Figure 1 [19]. The product was purified by column chromatography and further purification by several repetition of recrystallization from the mixture of ethanol and *n*-hexane.

The phase transition temperatures and enthalpies were detected by a Differential Scanning Calorimeter (TA Instrument, 2920 MDSC) and the textures of the mesophase were observed by a polarizing microscope (POM) (Olympus, BX-51) equipped with a hot stage (Mettler, FP80HT). Powder X-ray diffraction (XRD) studies were

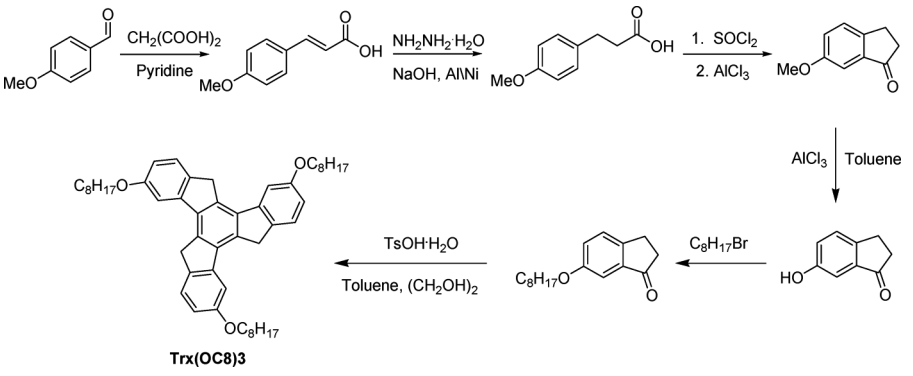

Figure 1. Synthetic Route of 2,7,12-trioctyloxytruxene (in short Trx(OC8)3).

carried out by using a Rigaku Geigerflex X-ray diffractometer (CuK_α) with a custom hotstage. The charge carrier mobility was measured by TOF method on a liquid crystal film sandwiched between Indium-Tin-Oxide covered glass plates. The cell thickness was approximately 15 μm, as determined by the interference pattern of the cell in the UV–visible spectrum. The cell was capillary filled in under an inert gas (Ar) after being degassed under vacuum by slowly cooling the sample from the isotropic liquid (Iso) state. No surface treatment was used in this study. The cell was set up in a hotstage equipped with a polarizing microscope and externally biased by a stabilized DC power supply. A N_2 laser ($\lambda = 337$ nm, 800 ps, $\varphi = 1$ mm) was used for a pulsed light irradiation. A transient photocurrent was detected by a digital oscilloscope (Hewlett Packard, HP54820A) with a variable-gain high-speed current amplifier (FEMTO, DHPCA-100).

3. Results and Discussion

3.1. *Phase Transition Behaviors*

DSC curves of Trx(OC8)3 is shown in Figure 2. On cooling process (bottom) by 0.5°C min^{-1}, there are two exothermic peaks corresponding to the transition between isotropic phase (I) and mesophase and crystallization at 131°C (3.4 kJ mol^{-1}) and 87°C (7.3 kJ mol^{-1}), respectively. Following on heating process (middle) by 0.5°C min^{-1}, Trx(OC8)3 shows two endothermic peaks corresponding to the transition crystal - mesophase and the isotropic melt at 118°C (37.9 kJ mol^{-1}) and 133°C (3.4 kJ mol^{-1}) in spite of the crystal - mesophase transition at temperature 88°C on 2nd heating at scanning rate of 10°C min^{-1} [19]. There was another broad exothermic peak around 80°C (20.7 kJ mol^{-1}). This implies that after cooling process it might be a metastable phase and forming more stable state causes an exothermic peak and 30°C

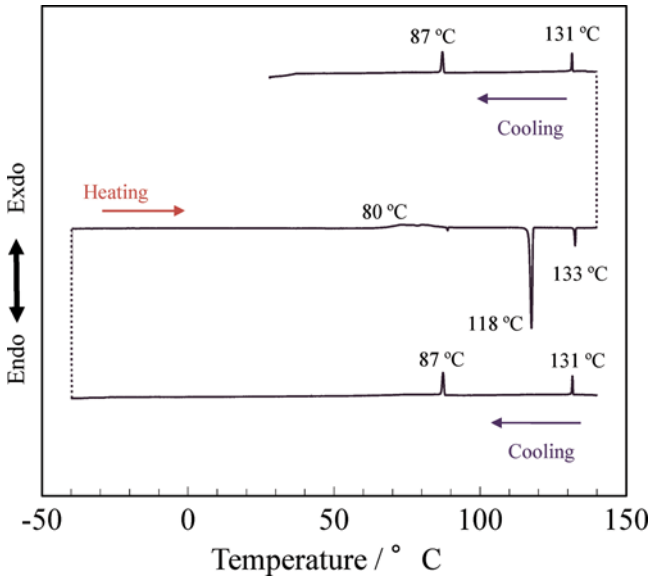

Figure 2. DSC curves of Trx(OC8)3 (heating and cooling rate; 0.5°C min^{-1}). (Figure appears in color online.)

higher shift of the phase transition temperature to the mesophase was observed. Indeed, the melting point of recrystallized sample was 118°C at a scanning rate of 5°C min^{-1}. The optical texture observation by POM at 10°C min^{-1} revealed that the phase transition at 88°C and 133°C which are the melting and clearing points, respectively. A typical fan-shaped texture was seen for the meophase, indicating a Col_h mesophase is formed.

3.2. *XRD Analysis*

XRD measurement for non-aligned sample was performed at 120°C in the mesophase. Figure 3 shows the XRD patterns of Trx(OC8)3. A set of reflections corresponding to d_{10}, d_{11} and d_{20} of which ratio in distance is 1: $1/\sqrt{3}$: 1/2 was observed and this is an evidence that hexagonal arrays of columns exist. Additional two reflections were observed at *ca.* 4.6 Å (broad halo) and *ca.* 3.6 Å (shoulder), which are assigned to the average distance of the molten alkyl chains and intracolumnar order, respectively. Shoulder reflection peak near 3.6 Å indicates the existence of the molecular stacking in intra columnar structure. The lattice parameter of the Col_h phase was calculated to be $a = 20.9$ Å and this value is almost 2/3 for the molecular diameter (*ca.* 31 Å) with fully extended chains and this is less than that of corresponding six-chain analogue (*ca.* 25 Å) [20]. This is reasonable that the reduced number of periphelal chains causes dense packing of columns in Col_h structure because the volume of aklylchains is decreased. Trx(OC8)3 exhibits a Col_h mesophase of which melting and clearing points are 118°C and 133°C, respectively. The reduced number of substituted alkyl chains leads to the decrease of thermal stability of Col_h mesophase in comparison to the corresponding six-chain analogue (melting: 86°C, clearing: >300°C) [20]. These results are consistent with the optical textures observed on cooling from the Iso.

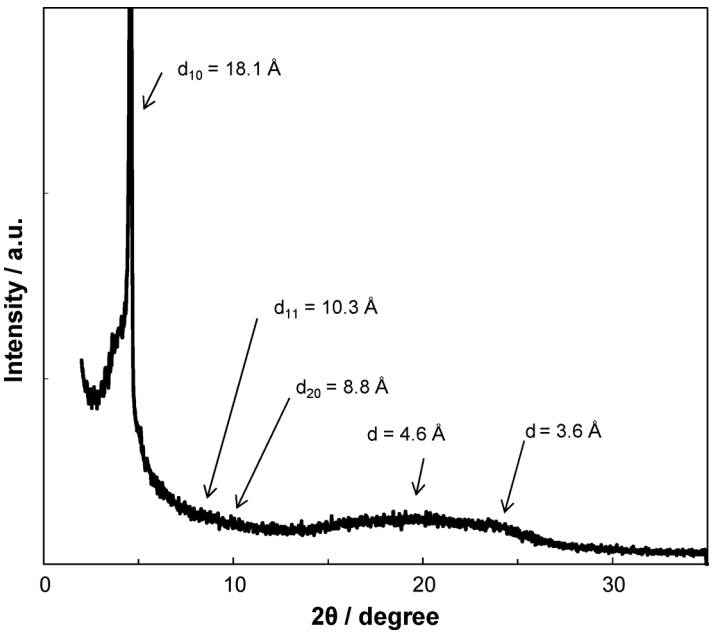

Figure 3. XRD pattern (powder) of Trx(OC8)3 at 120°C.

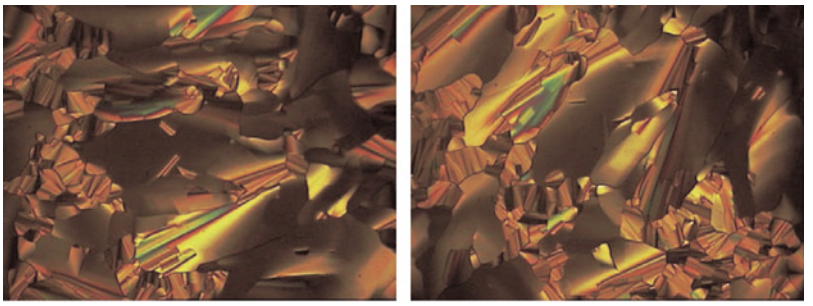

Figure 4. Polarizing microphotographs of the sample cell for 15.4 μm-thick cell at 120°C (a) before and (b) after rotation of the sample on the stage by 45°. (Figure appears in color online.)

3.3. *Charge Carrier Transport Property*

The transient photocurrent measurements have been performed by TOF technique for the partly homeotropically aligned area (Fig. 4) to investigate the charge transport along the columnar axis. Figure 5(a) and (b) show a typical transient photocurrent of Trx(OC8)3 (80°C, thickness 15.4 μm) for positive and negative carriers in the mesophase under various electric fields, respectively. A clear fast transit (arrows in Fig. 5) was observed which corresponded to the transport of positive and negative charge carriers by electronic process. The drift mobility for hole and electron are almost same value and in the range of $5 \times 10^{-2} \sim 1 \times 10^{-1}\,cm^2\ V^{-1}\ s^{-1}$ at a transit time range of microseconds without electric field dependence.

Figure 6 shows temperature dependence of the charge carrier mobility for positive and negative charge carriers on cooling process. Bipolar carrier transports were observed for Trx(OC8)3. The drift mobility measurements reveal it is in the order of $10^{-2}\,cm^2\ V^{-1}\ s^{-1}$ in the Col_h meophase and it increases to $10^{-1}\,cm^2\ V^{-1}\ s^{-1}$ at the Col_h - metastable phase transition and the value of mobility kept almost constant within the same phase. This implies truxene is an interesting molecular core for liquid

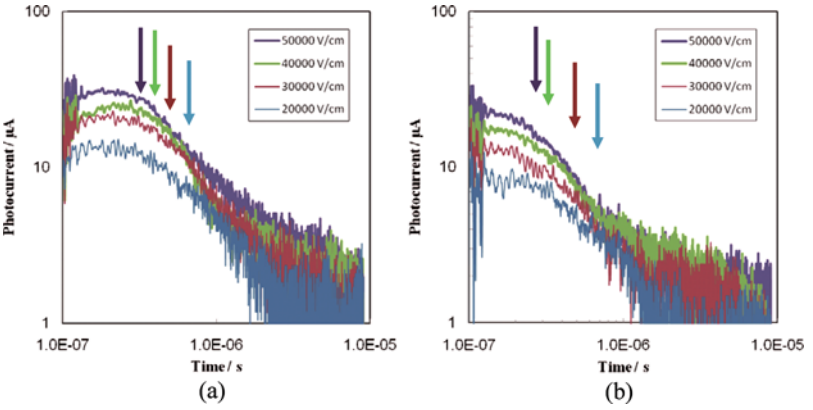

Figure 5. Log-log plots of transient photocurrent for (a) positive and (b) negative carriers of Trx(OC8)3 at 80°C on cooling process.

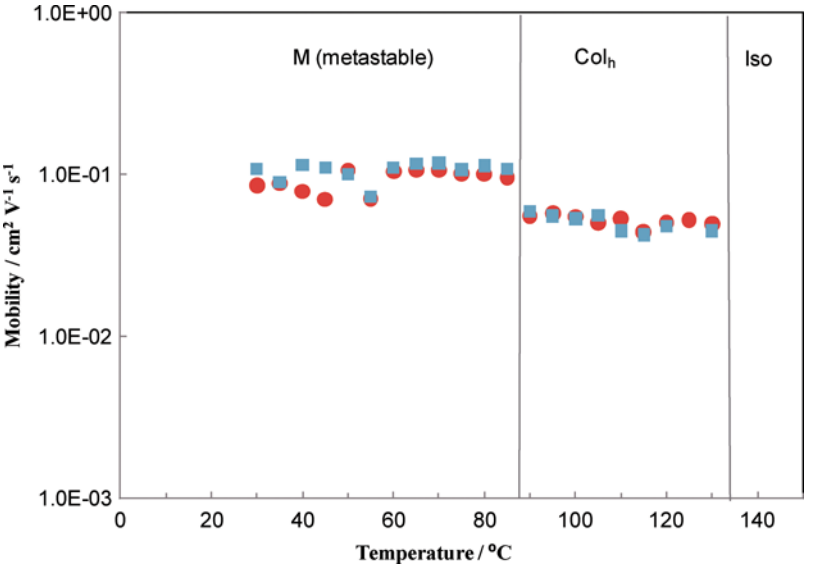

Figure 6. Temperature dependence of drift charge carrier mobility of Trx(OC8)3 for positive (circle) and negative (square) carriers. (Figure appears in color online.)

crystalline semiconductors. However, in fact, in order to obtain the ambipolar electronic carrier transport, it was needed careful purification of compound by means of repeated recrystallization. Furthermore, the hole drift mobility of the present sample was faster than that of previously reported [19]. It was probably due to the purity of the liquid crystalline sample used and the less impurities in the electric path in the bulk sample leads to the fast electronic carrier mobility [21]. These results imply purity of liquid crystalline semiconductor is one of the important issues to get fast charge carrier mobility.

4. Conclusions

A truxene DLC with three peripheral chains, Trx(OC8)3, exhibits a Col_h mesophase of which melting and clearing points are 118°C and 133°C, respectively. TOF measurements of charge carrier mobility in truxene DLC with three peripheral chains, Trx(OC8)3, were carried out and bipolar electronic carrier transports in the mesophase and lower metastable phase were observed. The drift mobility for hole and electron are almost same order and the value is $5 \times 10^{-2}\,cm^2\ V^{-1}\ s^{-1}$ in the Col_h mesophase and it increases to $1 \times 10^{-1}\,cm^2\ V^{-1}\ s^{-1}$ at the Col_h - metastable phase transition. These results indicate truxene is an interesting molecular core for liquid crystalline semiconductors.

Acknowledgment

This research was partly supported by Japanese Society for the Promotion of Science (JSPS) - the National Natural Science Foundation of China (NSFC) Joint Project (No. 50811140156).

References

[1] Adam, D., Closs, F., Frey, T., Funhoff, D., Haarer, D., Ringsdorf, H., Schumacher, P., & Siemensmeyer, K. (1993). *Phys. Rev. Lett.*, *70*, 457.

[2] Boden, N., Bushby, R. J., & Clements, J. (1993). *J. Chem. Phys.*, *98*, 5920.

[3] Adam, D., Schumacher, P., Simmerer, J., Haussling, L., Siemensmeyer, K., Etzbach, K. H., Ringsdor, H., & Haarer, D. (1994). *Nature*, *371*, 141.

[4] Iino, H., Hanna, J., & Haarer, D. (2005). *Phys. Rev. B*, *72*, 193203.

[5] Craats, A. M., Warman, J. M., Fechtenkötter, A., Brand, J. D., Harbison, A. M., & Mülen, K. (1999). *Adv. Mater.*, *11*, 1469.

[6] Iino, H., Takayashiki, Y., Hanna, J., & Bushby, R. J. (2005). *Jpn. J. Appl. Phys.*, *44*, L1310.

[7] Monobe, H., Mima, S., & Shimizu, Y. (2000). *Chem. Lett.*, *29*, 1004.

[8] Craats, A. M., Warman, J. M., Schlichting, P., Rohr, U., Geerts, Y., & Mülen, K. (1999). *Synth. Met.*, *102*, 1550.

[9] Sienkowska, M. J., Monobe, H., Kaszynski, P., & Shimizu, Y. (2007). *J. Mater. Chem.*, *17*, 1392.

[10] Nakayama, H., Ozaki, M., Schmidt, W. F., & Yoshino, K. (1999). *Jpn. J. Appl. Phys.*, *38*, L1038.

[11] Monobe, H., Okamoto, S., & H. EnomotoShimizu, Y. (2007). *Mol. Cryst. Liq. Cryst.*, *476*, 277.

[12] Hirai, Y., Monobe, H., Mizoshita, N., Moriyama, M., Hanabusa, K., Shimizu, Y., & Kato, T. (2008). *Adv. Funct. Mater.*, *18*, 1668.

[13] Monobe, H., Okamoto, S., Enomoto, H., & Shimizu, Y. (2010). *Jpn. J. Appl. Phys.*, *49*, 01AF04.

[14] Sergeyev, S. W., & PisulaGeerts, Y. (2007). *Chem. Soc. Rev.*, *36*, 1902.

[15] Shimizu, Y., Oikawa, K., Nakayama, K., & Guillon, D. (2007). *J. Mater. Chem.*, *17*, 4223.

[16] Iino, H., Hanna, J. (2005). *Opto-Electron. Rev.*, *13*, 295.

[17] Sun, Y., Xiao, K., Liu, Y., Wang, J., Pei, J., Yu, G., & Zhu, D. (2005). *Adv. Funct. Mater.*, *15*, 818.

[18] Iyoda, K., Yasuda, T., & Kato, T. (2009). *Chem. Asian. J.*, *4*, 1619.

[19] Zhao, K., Chen, C., Monobe, H., Hu, P., Wang, B., & Shimizu, Y. (2011). *Chem. Commun.*, DOI: 10.1039/C1CC10299K.

[20] Foucher, P., Destrade, C., Huu Tinh, N., Malthete, J., & Levelut, A. M. (1984). *Mol. Cryst. Liq. Cryst.*, *108*, 219.

[21] Hanna, J. (2005). *Opto-Electron. Rev.*, *13*, 259.