<table>
<thead>
<tr>
<th><strong>Title</strong></th>
<th>Binary systems of discotic liquid crystalline semiconductors toward solution-processing thin film devices</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Author(s)</strong></td>
<td>Shimizu, Y.; Matsuda, Y.; Nekelson, F. et al.</td>
</tr>
<tr>
<td><strong>Citation</strong></td>
<td>Proceedings of SPIE - the International Society for Optical Engineering. 2012, 8279, p. 82790G-1-82790G-8</td>
</tr>
<tr>
<td><strong>Version Type</strong></td>
<td>VoR</td>
</tr>
<tr>
<td><strong>URL</strong></td>
<td><a href="https://hdl.handle.net/11094/75929">https://hdl.handle.net/11094/75929</a></td>
</tr>
<tr>
<td><strong>rights</strong></td>
<td></td>
</tr>
<tr>
<td><strong>Note</strong></td>
<td></td>
</tr>
</tbody>
</table>
Binary Systems of Discotic Liquid Crystalline Semiconductors toward Solution-Processing Thin Film Devices

Y. Shimizu* a, Y. Matsuda a,b, F. Nekelson a,c, Y. Miyake a,c, H. Yoshida b, A. Fujii b and M. Ozaki b

a Synthetic Nano-Function Materials Group, Research Institute for Ubiquitous Energy Devices, National Institute of Advanced Industrial Science and Technology, Kansai Center (AIST-Kansai), Midorigaoka, Ikeda, Osaka 563-8577, JAPAN;
b Department of Materials Chemistry, Faculty of Science and Engineering, Ryukoku University, Seta, Otsu, Shiga 555-0000, JAPAN;
c Division of Electrical, Electronic and Information Engineering, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka, 565-0871, JAPAN

ABSTRACT

Binary mixtures of a phthalocyanine (Pc) mesogen and its Zn complex, which have eight decyl chains at the non-peripheral positions of Pc were studied as an organic semiconducting system. The complete miscibility was observed for the Colh mesophase and the carrier mobility for the Colh mesophase was measured to give small decrease of mobility in the 1:1 mixture in comparison to that of the pure compounds. These indicate that in this binary system, two compounds could mostly behave as the identical molecules and no specific interaction was expected. The different component ratio affects the carrier mobility depending on the ratio, meaning the molecular dispersion is not taken place in a monomolecular level and possibly columns formed by each compound exist to hold a certain distance for successive charge hopping. These results indicate that the mixture of mesogens could make mesogenic systems useful for new applications such as organic thin film solar cells.

Keywords: liquid crystalline semiconductor, phthalocyanine, carrier mobility, printed electronics, organic solar cell

1. INTRODUCTION

Organic electronics is one of the most interesting and important research fields for ubiquitous electronic devices and it is expected that light-weight and flexible electronic devices are realized in commercial base. Recent trend of researches have insisted the solution processing of organic thin film devices such as OLED [1], OFET [2] and organic thin film solar cells [3] are promising in terms of low-cost production of the devices. The organic semiconductors applicable for so-called “Printed Electronics” are required to have some properties such as high solubility into common organic solvents, spontaneous alignment of molecules during the solvent evaporation to form a high quality of thin film on a substrate, which surely leads to the better performance of devices. Therefore, a self-assembling nature of molecules should be a profoundly related and attractive property for organic semiconductors suitable for “Printed Electronics”. This background has made it so interesting to study “organic semiconductors with liquid crystalline properties” because all these requirements are in fact, facilitated properties in liquid crystalline materials as seen in the strong tendency to form the larger uniform domain as an example [4,5].

The discovery of high carrier mobility in mesophase[6] gave an impact to liquid crystal studies and its comparable value to that of a-silicon (> 10⁻¹ cm² V⁻¹ s⁻¹) means that liquid crystalline semiconductor also is a promising candidate for “Printed Electronics”. It is a kind of surprise to see such a high mobility in mesophase where the molecules, more or less, are mobile and/or being fluctuated as a dynamic state of matter. Therefore, liquid crystals could open a new field of research in organic electronics and have been so extensively studied in recent years. [7]. Unfortunately, such dynamic state of molecularly ordered materials have never led to the higher mobility so far than those of poly-crystalline and single crystalline thin films of organics such as pentacene [8], rubrene [9] and diphenylanthracene [10] with the far lower...
solubility into organic solvents. However, it was recently found that the crystalline films of liquid crystalline semiconductors tend to show the higher mobility in thin-film transistors.\[4,5,11\]

The molecular shapes of mesogens are anisotropic and the typical molecular shapes are of “rod-like (calamitic) and “disc-like”(discotic). The smectic layered and molecularly stacked columnar structures are essentially important orderings of molecules, respectively, as charge transport materials by an electronic process. Columnar structure of columnar mesophase is the similar motif to quasi-one-dimentional conductors of aromatic compounds and their metal complexes\[12\] in which charges on molecules are likely to transport along the axis of molecular stacking. This molecular order is essentially important as a path of electronic hopping even for disordered states of matter. An important thing is the fact that it would be possible to control the molecular alignment of columnar mesophase\[13\] and in the case of hexagonal columnar (Colh) mesophase one can easily obtain its homeotropic alignment where the molecularly stacking columns align perpendicular to the substrate surface.\[14\] This “homeotropic alignment” is important for thin film solar cells, where the semiconducting active layer is sandwiched by electrode substrates.

Recently, Iino et al. found that 1, 4, 8, 11, 15, 18, 22, 25-octaoctylphthalocyanine (C8PcH2) exhibits an ambipolar nature for the mobility in the hexagonal disordered columnar (Colhd) mesophase, while phthalocyanine (Pc) is recognized as a p-type semiconductor \[15\]. Also the mobilities are rather fast in the order of $10^4 \, \text{cm}^2 \, \text{V}^{-1} \, \text{s}^{-1}$, exhibiting field-independent property and a slight or non-dependency on temperature which are of typical for liquid crystalline semiconductors\[16\]. We reported ambipolar nature of carrier mobility with so high drift mobility for the poly-crystalline films (1.4 cm² V⁻¹ s⁻¹) of the hexyl homologue (C6PcH2) as shown in Fig.1.\[17\] Also C6PcH2 was applied to thin film solar cells as a p-type semiconductor for the bulk heterojunction system with PCBM to give a rather high performance as organic solar cells, where the semiconducting active layer is sandwiched by electrode substrates.

Phthalocyanine (Pc) is a well-known material for pigments and dyes. Therefore, it strongly absorbs the light in the visible wavelength range and thus, it is the reason why Pc is widely used as p-type semiconductor in the studies of organic thin film solar cells. Another important property of Pc molecules is the fact that Pc molecule could form metal complexes with a variety of metal species. This means Pc is the molecule exhibiting light harvesting properties for wide range of wavelength by chemical modifications and metal chelations.

On the other hand, “miscibility” is one of the characteristic properties of liquid crystals. Two different liquid crystalline molecules which exhibit the identical liquid crystalline phase in thermodynamical point of view could be mixed at a molecular level to exhibit the identical liquid crystalline phase at any component ratio, if the mixing does not induce any additional intermolecular interactions. Contrast to this, “phase separation” is also a character easily emerged in liquid crystals because of the dynamic state of matter. These two characters are significantly important for spontaneous formation of hierarchical structures in molecular blends. Interdigitated geometries of p- and n-types of
semiconductors is being proposed as an ideal structure for high performance of bulk heterojunction active layer (Figure 3) and self-assembling nature of liquid crystals is an important character to realize a spontaneous formation of such a structure.

In this communication, some results on miscibility and carrier transport properties of a binary system consisting of a non-peripheral octadecylphthalocyanine (C10PcH2) and the Zn complex (C10PcZn) both of which exhibit a hexagonal columnar (Colh) mesophase.

2. EXPERIMENTAL

2.1 Syntheses and purifications of the compounds

C10PcH2 was synthesized according to the literature with slight modifications and C10PcZn was prepared by chelating reaction of C10PcH2 with zinc acetate. The products were fully purified by column chromatography (Silica-gel with toluene as eluent) followed by the repetitive recrystallization from toluene - methanol (1:2) solution with chelating reagent treatments.
2.2 Characterization of mesomorphism

The phase transition temperatures and enthalpy changes were measured by differential scanning calorimetry (DSC, TA instrument DSC2920) and from microscopic observations of the optical textures (Olympus BH2 and Mettler FP90 hot stage). The mesophases were identified by X-Ray diffraction in the temperature range of the mesophase using a Rigaku RINT 2000 equipped with a hand-made hot stage.

2.3 Charged carrier mobility of mesophase

The mobility in mesophase was determined by Time-Of-flight (TOF) technique as schematically shown in Fig. 4.\cite{22}

The cell is of sandwich-type consisting of two ITO-coated glass plates as the electrodes (effective area of the electrode: 5mm x 5mm) and polyimide film (Toray Kapton® with 12.5 μm) as spacer. The actual cell gaps were evaluated by an interference technique of light transmittance. The sample was injected by capillarity action at the temperature above the isotropization one. A N2-pulsed laser (337 nm, 800 ps) was used for the photocarrier generation. The bias was applied by a DC power supply (WF1941). The transient photocurrents were detected by a digital oscilloscope (HP, infinum) with the help of a wide band preamplifier (NF electronics instruments, BX-31A). The mobility, $\mu$, was calculated by the equation below,

$$\mu = \frac{d^2}{V \tau_s}$$

where $d$ is the sample thickness, $V$ the applied bias and $\tau_s$ the transit time.

![Figure 4: A schematic drawing of Time-Of-Flight (TOF) apparatus equipped with a polarized microscope.](image)
3. RESULTS AND DISCUSSION

3.1 Miscibility

Fig. 5 shows a binary phase diagram of C10PcH2 and C10PcZn. One can see a complete miscibility for the Colh mesophase because one can see a linear correlation for the clearing point. This indicates two species of molecules are dispersed in a molecular level and no strong intermolecular interactions take places by mixing.

On the other hand, the melting line is approximately linear connecting between two melting points of C10PcH2 and C10PcZn. This may indicate that the mixture forms a kind of solid solution in the crystalline solid. The powder XRD studies indicate that in this crystalline phase of the mixtures has the similar arrangement of molecules to that in the Colh mesophase, meaning hexagonal arrays of columns are still remained.

3.2 Carrier mobility

Fig. 6 shows temperature dependence of mobility for C10PcZn and C10PcH2. One can see both compounds, C10PcH2 and C10PcZn exhibit an ambipolar nature like the case of C8PcH2 and C6PcH2, though no clear photocurrent decay curves could not be obtained for the crystal phases of both C10 compounds in the TOF measurements. This situation is similar to that of C8PcH2. Also field-independent mobilities are seen for both hole and electron, which is typical shown in liquid crystalline semiconductors. Both compounds tend to spontaneously align in a homeotropic way for the Colhd phase on cooling from the Iso phases between glass and ITO-coated glass substrates and this is the similar tendency to C10- and C8-PcH2. The mobility of C10PcZn exhibits temperature dependence in the Colh mesophase, while it gets less in the Colr mesophase. However, the mobilities of hole and electron are in the order of $10^{-1}$ cm$^2$ V$^{-1}$ s$^{-1}$ which go up to 0.44 cm$^2$ V$^{-1}$ s$^{-1}$ for hole and 0.36 cm$^2$ V$^{-1}$ s$^{-1}$ for electron. C10PcH2 exhibit a weak temperature dependence of mobility.

![Figure 5: A binary phase diagram of C10PcH2-C10PcZn mixture.](image)

![Figure 6: Temperature dependence of carrier mobility for (a) C10PcZn and (b) C10PcZn. Field strength: 17.8 kVcm$^{-1}$.](image)
for hole and electron and the mobilities are in the order of $10^{-1}$ cm$^2$ V$^{-1}$ s$^{-1}$. Interestingly for C6PcH2, C10PcH2 and C10PcZn, the electron mobility is higher than the hole one. Unfortunately it was so difficult to determine the mobilities in the crystalline solid phases due to the dispersive photocurrent decay curves.

On the other hand, the mixtures were also studied on their properties of carrier transport by TOF technique. For the Col$\beta$ mesophase of the mixtures also a strong tendency for spontaneous homeotropic alignment was observed in the cells (ITO-ITO sandwich-type). Fig. 7 shows the temperature dependence of hole and electron mobilities of the 1:1 mixture. It was found that the both mobilities are reduced to the order of $10^{-2}$ cm$^2$ V$^{-1}$ s$^{-1}$. However, this is not so drastic drop of mobility, considering that the charge transfer rate between two molecules of which HOMO and LUMO energy levels are different is strongly affected by the energy gaps to provide somehow shallow traps and recombination sites. Therefore, the fact that the reduced mobility is in the order of $10^{-2}$ cm$^2$ V$^{-1}$ s$^{-1}$, decreasing mobility within 1/10 indicates that a certain length of successive charge hopping path is still maintained even after mixing these two columnar mesogens. In other words, columns formed by C10PcH2 and by C10PcZn, independently, are coexisting as segregated columns (not alternative stacks of two types of mesogens) to play a role of electronic hopping path. Interestingly, the mobilities could be determined for the crystalline solid phase, while those could not for the crystal phases of pure compounds due to the dispersive curves of photocurrent and this may indicate that the crystalline solid phase is of disordered affected by the mesophase order in the Col$\beta$ mesophase.

Recently it was reported that the addition of C6PcH2 into the bulk heterojunction system of P3HT/PCBM leads to the enhancement of solar cell function and the added C6PcH2 plays a role of additional charge generator.\[23]\n
This indicates that C6PcH2 molecules are phase-separated as columns and these columns are penetrated into the P3HT/PCBM heterointerfaces. The resent results shown in this communication could provide some evidences for the possibility to utilize “miscibility of columnar mesophases” involving “appropriate segregation of columns” toward the better performance of bulk heterojunction-type organic solar cells.

4. CONCLUSION

It was found that C10PcH2 and C10PcZn exhibit a complete miscibility in the Col$\beta$ mesophase. The XRD results indicate that the crystalline state of the mixture form a solid solution with a hexagonal order of columns. The hole and electron mobilities of the Col$\beta$ mesophase in the 1:1 mixture are reduced in comparison to those of the pure compounds. The mobilities of hole and electron decrease to be in the order of $10^{-2}$ cm$^2$ V$^{-1}$ s$^{-1}$, whilst the pure compounds exhibit the mobilities in the order of $10^{-1}$ cm$^2$ V$^{-1}$ s$^{-1}$. These results indicate that the mixture exhibits a Col$\beta$ mesophase in which the columns of C10PcH2 and C10PcZn coexist independently to some extent as a thermodynamically stable state of molecular aggregation. Therefore, it is possible to prepare a p-type of semiconducting mixture without any drastic reduction of carrier mobility and this could be realized based on the miscibility as a characteristic property of liquid crystals. And it also implies that with a variety of mesogen of which molecular shape and mesophase are identical to each, it is possible to develop a p-type semiconducting system of which wavelength of light harvest gets wider against one n-type semiconductor such as PCBM.
ACKNOWLEDGMENTS

This study was carried out by a financial support, in part by JST-ALCA (Japan Science and Technology Agency, Advanced Low Carbon Technology Research) Program. FN and YMi thank Photonic Research Center, Osaka University and Osaka University Frontier Research Center (the 8 Global Center of Excellence (Global COE) Program “Center for Electronic Devices Innovation” at Osaka University), respectively. YMa acknowledges to Prof. Kingo Uchida in Ryukoku University for providing this opportunity to study on mesophase semiconductors in AIST-Kansai for his graduate thesis.

REFERENCES


*yo-shimizu@aist.go.jp; phone 81 72 751-9525; fax 81 72 751-9628*