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Miscibility and Phase Separation in LC Semiconductor Blends

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ABSTRACT

Binary blends of phthalocyanine (Pc) LCs, 1, 4, 8, 11, 15, 18, 22, 25-octadecylphthalocyanine (C10PcH₂) and the corresponding Zn complex (C10PcZn) were studied which have the identical hexagonal columnar (Col_h) mesophase and the same order of carrier mobility ($\sim 10^{-1} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) in the mesophase. The phase diagram shows a complete miscibility in the Col_h mesophase and no eutectic point was detected. The carrier mobility evaluated by Time-Of-flight (TOF) technique goes down to $10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in Col_h phase of the initial blends prepared by solution mixing. However, the treatment of these binary systems with repetitive heating and cooling gives recovering of carrier mobility to the original level, though their HOMO and LUMO levels are slightly different in these two mesogenic Pcs. These results indicate that two types of single component column form a hexagonal array in mesophase. Also the blends with PCBM were studied on carrier mobility as well as miscibility and phase separation.

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

1. INTRODUCTION

“Miscibility” is one of the characteristic properties of liquid crystal. Two liquid crystalline compounds exhibiting the identical liquid crystalline phase in thermodynamical point of view could be mixed at a molecular level to form the identical liquid crystalline phase at any component ratio. This requires a condition that the mixing does not induce any additional intermolecular specific interactions. On the other hand, “*phase separation*” is also a phenomenon easily emerged in liquid crystal because of the dynamic state of molecular aggregation where mesogenic molecules form single-component domains in a separate way and/or part by part to each component. These two properties are significantly important for spontaneous formation of hierarchical or periodical structures in molecular blends. In other word, *miscibility* and *phase separation* are strongly useful tools for constructing complex structures of molecular aggregation and therefore, it should be based on the molecular design for expecting functional properties such as bulk heterojunction (BHJ) active layer in organic photovoltaics (OPV).

When one prepares the blend with two mesogenic compounds exhibiting, for example, nematic phase, one can make a binary phase diagram showing *miscibility* and a typical diagram is shown in Fig.1. At any component ratio, one sees a temperature range of nematic phase. Two clearing points of the compounds can be connected with a straight line as an ideal manner, while the both melting points decreases to give an eutectic point at a component ratio, which is, in principle, predicted with Le Chatelier-Schröder equation (Eq. 1 & 2). At the eutectic point, the widest range of temperature is seen for LC phase, meaning that the temperature range of LC phase can be extended by mixing two mesogenic compounds. This has been utilized to control the temperature range of LCs in display applications.

$$-(\Delta H_A / R) (1/T - 1/T_A) = \ln X_A \quad (1)$$

$$-(\Delta H_B / R) (1/T - 1/T_B) = \ln X_B \quad (2)$$

$$X_A + X_B = 1$$

X_A, X_B : component ratios of compound A and B

For discotic columnar mesophase, *miscibility* is more sensitive to molecular size and intermolecular interaction than for calamitic lower ordered phases.^[1] In highly ordered mesophase, miscibility condition is less allowed. However, it is not so simple for the case of organic semiconductor. For a mixture in which two compounds have the difference in the electronic level (HOMO and LUMO), the carrier mobility is decreased because two compounds meet directly in molecular level.^[2] Hopping conduction is seriously depressed. This means that the structure (molecular order) of such a mixture should be controlled to avoid this electronic interference to keep at least the original level of carrier mobility for each compound. Therefore, two compounds that should be mixed to fabricate a thin film active layer in device make its molecular order independently without electronic interference. This would be realized in a way of *phase separation*. Generally, chemical structure of discogen shows a combination of rigid aromatic core and flexible tails peripherally attached to the core, like a nano-wire in an electronic point of view. In columnar stacks of discogenic molecules, the center of column is occupied with stacking aromatics forming an electronic charge transport path and is covered with insulating alkyl chains. Considering this characteristic image of columnar structure, one can expect that if single component columns for two discogens form a columnar mesophase with a dispersion of columnar level, it would not cause the depression of charge transport efficiency.

When 1D-charge transport takes place along the columnar axis and the axis aligns in a perpendicular way (homeotropic alignment) to the substrate,^[3] this geometry of sandwich-type cell is good for thin film solar cell.^[4] In the active layer of organic thin film solar cell, p- and n- type of semiconductors are mixed to give p/n heterojunction where charge separation takes place to generate hole and electron following migration of excitons generated by photoabsorption. In a BHJ active layer, exciton migration path, p/n heterojunction, and charge transport path have to be designed and fabricated. Furthermore, such a structure should be spontaneously formed. Especially, it is strong requirement in *Printed Electronics*. Most of BHJ-OPV studies reported so far have not yet clarified the structure of p/n junction in the layer as polymer semiconductors are used. In other words, it has not been controlled in a molecular level. The nano-scale structure in BHJ layer would be accessible by use of small molecule semiconductors. In particular, self-organization property of small molecules should be essentially important in terms of spontaneous formation of structure.

Recent studies on BHJ-type organic solar cells propose that interdigitated geometries of p- and n-types of semiconductors should be promising to attain the higher performance as OPV cells (Fig. 2)^[5] and self-assembling nature of liquid crystals should be important and useful character to realize a spontaneous formation of such a structure.

On the other hand, phthalocyanine is one of the trustful molecule in practical application as pigment and dye and has been studied as a semiconductor for organic photovoltaics due to its strong photoabsorption in visible region.

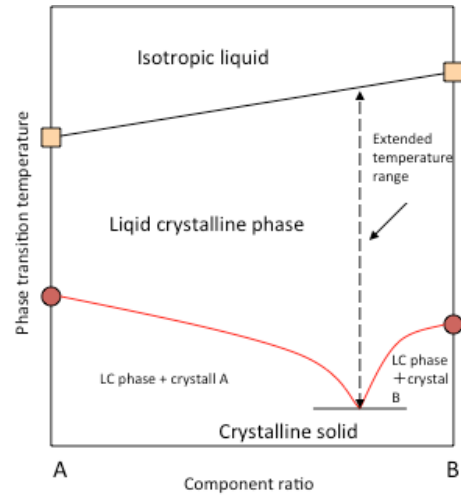


FIGURE 1 : A Typical model of a binary phase diagram of LCs (A and B). The extended temperature range is attained

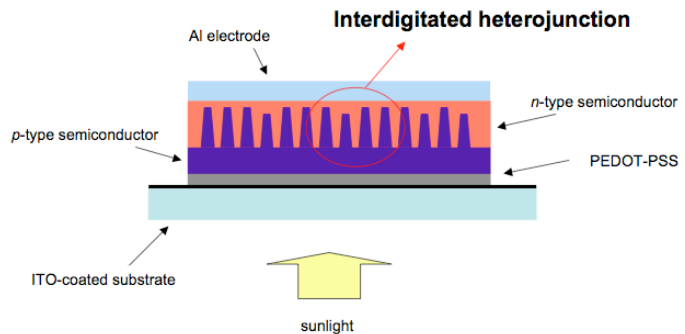


Figure 2: A schematic drawing of a proposed interdigitated structure of a bulk heterojunction active layer in organic thin film solar cells.

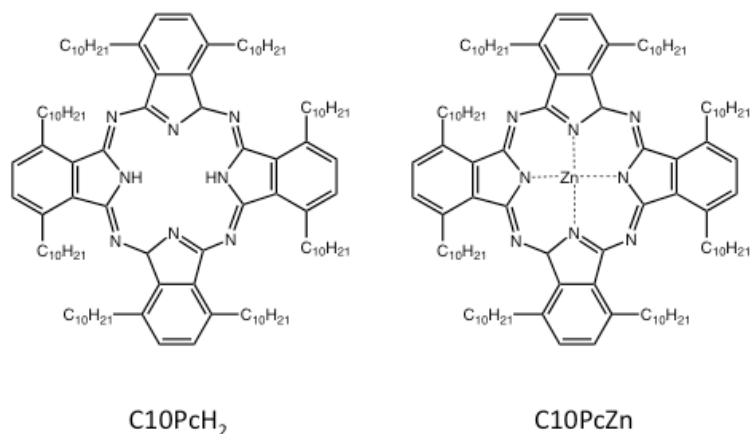


FIGURE 3 : Chemical structures of C10PcH₂ and C10PcZn used in this work and their phase transition sequences.

Recently, Iino et al. found that 1, 4, 8, 11, 15, 18, 22, 25-octaoctylphthalocyanine (C8PcH₂) exhibits an ambipolar nature of charge transport in the hexagonal disordered columnar (Col_{hd}) mesophase, while phthalocyanine (Pc) is recognized as a p-type semiconductor^[6]. Also the mobilities are rather fast in the order of 10⁻¹ cm² V⁻¹ s⁻¹, exhibiting field-independent property and a slight or non-dependency on temperature which are of typical for liquid crystalline semiconductors^[7]. 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).^[8] Also C6PcH₂ was applied to thin film solar cells as a p-type semiconductor for the bulk heterojunction system with PCBM ([6,6]-phenyl C₇₁ butyric acid methyl ester) to give a rather high performance as solution-processed organic solar cells with low molecular weight organic semiconductors (power conversion efficiency: 3.1 %, external quantum efficiency: >70% at the Q-band).^[9] Also the addition of C6PcH₂ into conventional P3HT/PCBM system was found to give the better performance due to the better light harvesting which was ascribed to the strong photoabsorption of Pcs.^[10]

In this communication, *miscibility* of two phthalocyanine LCs (C10PcH₂ and C10PcZn) were studied and the carrier mobility was measured by TOF technique to discuss the mixing status in both columnar and crystalline solid phases. It is worthwhile to notice that an 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 a molecule that could exhibit rich light-harvesting properties due to the wide range of wavelength that could be attained by chemical modifications and metal ligations. Therefore, it is an important notice that blending some of phthalocyanine compounds leads to the better light-harvesting ability toward organic photovoltaics.

The phthalocyanine LCs used in this work are of non-peripheral type as shown in Fig. 3. The connecting position of alkyl tails to phthalocyanine ring is not commonly seen most peripheral site. Therefore, steric problem gets remarkable when the molecules stack to form a columnar structure. In fact, even for the shorter homologue such as C6PcH₂, no evidence could be detected in X-ray diffraction measurements for the presence of stacking periodicity along the columnar axis. The phase sequence is shown in Table 1. Both C10PcH₂ and C10PcZn exhibit hexagonal columnar (Col_h) mesophase^[11] and the charge transport is ambipolar similar to C6 and C8PcH₂.

Table 1 Phase transitions of C10PcH₂ and C10PcZn

compound	phase transition				
C10PcH ₂	Cryst	87 °C (58 kJ/mol)	Colh	131 °C(8.6 kJ/mol)	Iso
C10PcZn	Cryst	94 °C (82 kJ/mol)	Colr	132 °C (-)	Colh 232 °C (15 kJ/mol) Iso

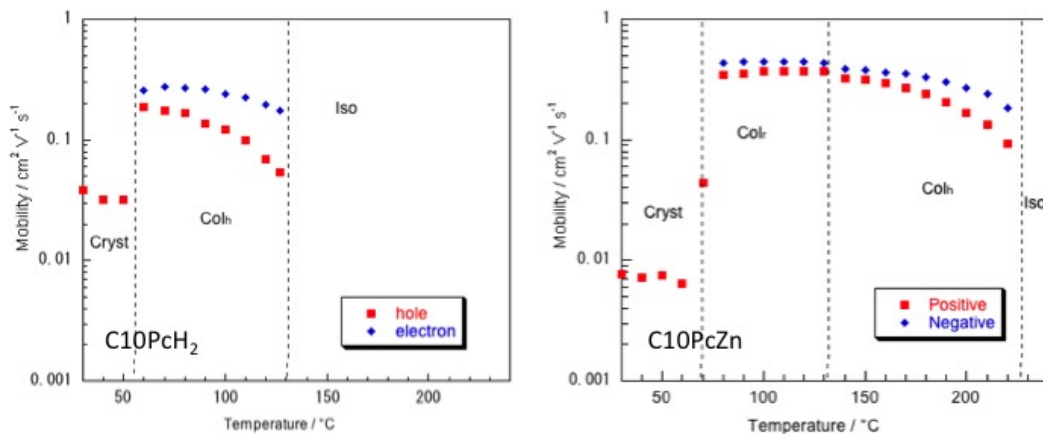


FIGURE 4 : Temperature dependence of hole and electron mobilities for C10PcH₂ and C10PcZn. Applied field : 10 kV cm⁻¹.

Temperature dependence of carrier mobility for C10PcH₂ and aaC10PcZn are shown in Fig. 4. Both hole and electron mobilities are temperature-dependent and the mobility decreases as temperature goes up. The carrier mobility is in the order of 10⁻¹ cm² V⁻¹ s⁻¹ in the Col_h mesophase, which is the same order for the Col_h mesophase of other homologues (C8 and C6). Interestingly for C6PcH₂, C10PcH₂ and C10PcZn, the electron mobility in the Col_h mesophase is higher than the hole one.

2. EXPERIMENTAL

2.1 Syntheses and purifications of the compounds

C10PcH₂ was synthesized according to the literature with slight modifications^[11] 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. For C10PcH₂, treatments with a chelating reagent was carried out to remove contaminant ionic metal species. The purity of compounds was checked by TOF measurement to see the saturation of transient photo-current decay curves as well as their carrier mobility. Purification process is so important as it affect the resultant photo-decay curves and carrier mobility.^[12]

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 carrier mobility in mesophase and crystalline phase was determined by Time-Of-flight (TOF) technique.^[13] 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 compound was injected by capillarity action at the temperature above the isotropization. A N₂-pulsed laser (337 nm, 800 ps) was used for the photocarrier generation. The transient photocurrents were detected by a digital oscilloscope (HP, infimum) with the help of a wide band preamplifier (NF electronics instruments, BX-31A). The mobility, μ was calculated by the equation below,

$$\mu = d^2 / V\tau_s$$

where d is the sample thickness, V the applied bias and τ_s the transit time.

Both compounds tend to spontaneously align in a homeotropic way for the Col_{hd} 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.

3. RESULTS AND DISCUSSION

3.1 Miscibility

Fig. 5 shows a binary phase diagram of C10PcH₂ and C10PcZn. One can see a linear correlation for the clearing point and the Col_h mesophase is observed at any component ratio. This indicates that two species of molecules are dispersed in a molecular level and no strong and additional intermolecular interactions take place by mixing. Consequently, complete miscibility is observed, though the clearing enthalpy values of these compounds show a certain difference (8.6 kJ/mol and 15 kJ/mol for C10PcH₂ and C10PcZn, respectively).

On the other hand, the melting line is approximately linear and no sign is found for the eutectic drop in temperature. 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 Col_h mesophase, meaning hexagonal arrays of columns are still remained, though the phase transition enthalpies show a certain gap (58 kJ/mol and 82 kJ/mol for C10PcH₂ and C10PcZn, respectively).

For the miscibility shown in C10PcH₂ / C10PcZn system, one can postulate two extreme situations of molecular blend. One is a simple molecularly dispersive system of C10PcH₂ and C10PcZn and another is a blend of single-component columns forming hexagonal array of columns in a segregated way (Fig. 6).

3.2 Carrier mobility

Fig. 7 shows temperature dependence of carrier mobility for C10PcZn/C10PcH₂ system. The carrier mobility gets lowered in the blends. Temperature dependence of carrier mobility in the Col_h mesophase is weakly temperature-dependent and it is in the order of $10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. For the Col_h mesophase of the mixtures also a strong tendency for spontaneous homeotropic alignment was observed in the cells (ITO-ITO sandwich-type).

It was found that the both hole and electron mobilities are reduced to the order of $10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. However, this is not so drastic decrease 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 shallow traps and recombination sites. In fact, photoelectron spectroscopy measurements of C10PcZn and C10PcH₂ revealed that HOMO and LUMO

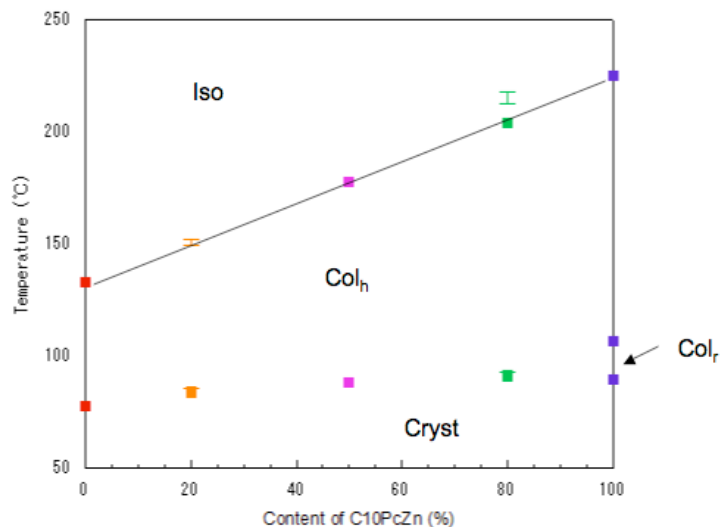


FIGURE 5 : A binary phase diagram of C10PcH₂-C10PcZn.

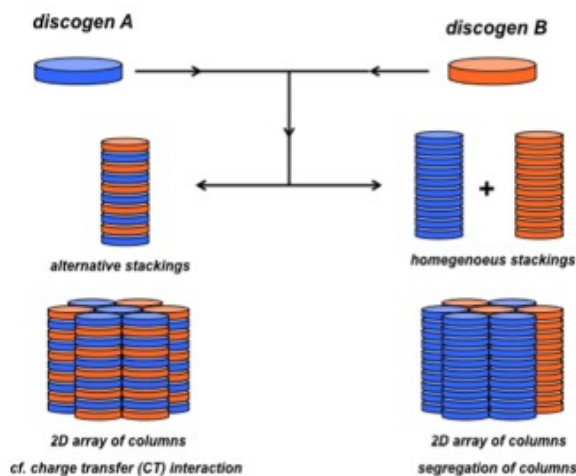


FIGURE 6: A schematic diagram of two situations of hexagonal columnar arrays for the blend.

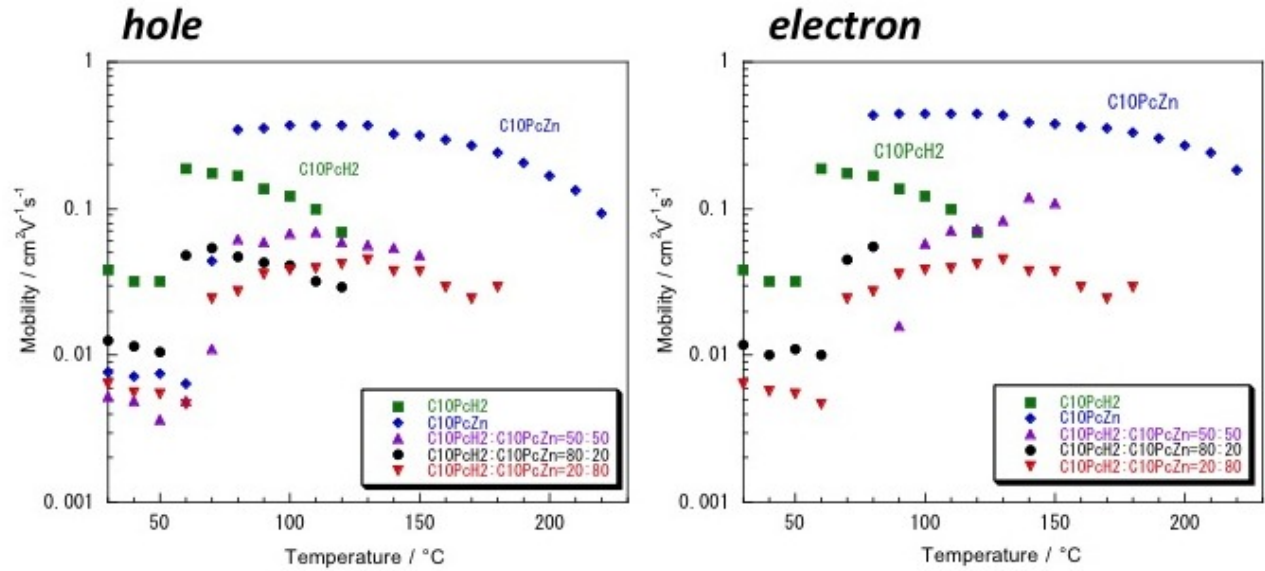


FIGURE 7 : Temperature dependence of carrier mobility for C10PcH₂, C10PcZn and the blends. Applied field : 10 kV/cm.

levels of C10PcZn are -5.15 and -3.53 eV, respectively and -5.03 and -3.51 eV for C10PcH₂, respectively. This means that C10PcZn could behave as a weak electronic acceptor and C10PcH₂ as a donor in this blend. Therefore, the fact that the reduced mobility in the order of 10⁻² cm² V⁻¹ s⁻¹ indicates that a certain length of successive charge hopping path is still maintained even after mixing these two columnar mesogens. However, contamination of one compound in a column of the counterpart disogen surely takes place.

The blends prepared by removing the solvent under a reduced pressure sometimes show a complicated phase transition curve on the 1st heating in DSC measurements. The second and third heating runs in heating and cooling cycles show a steady state of phase transition curve, meaning that the better mixing could be attained by repetitive cooling and heating treatments of blends.

The observed mobility shown in Fig. 7 was also variant by repetitive heating and cooling operations around the clearing point. As the number of cyclic operation is increases, the observed carrier mobility goes up to the original level shown by the single component samples as shown in Fig. 8. This result imply that segregated columns with the single

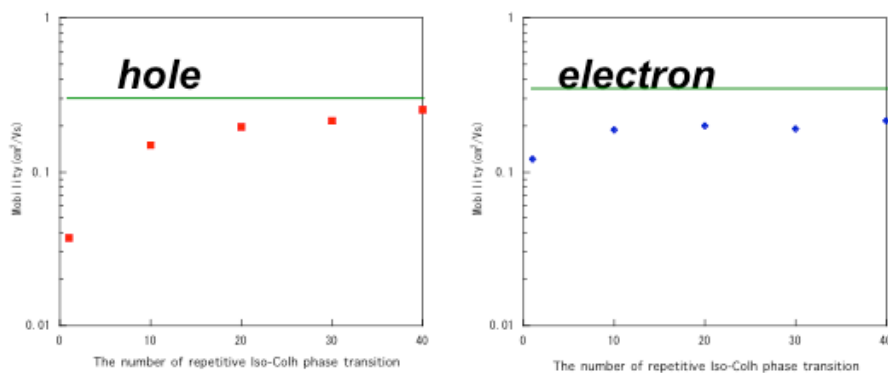


FIGURE 8 : Hole and electron mobilities vs. the number of heating and cooling cycle treated around the clearing point for the TOF cell with a C10PcH₂ / C10PcZn blend with 1:1 molar ratio. Measured at 165 °C (Col_h mesophase). The horizontal line indicates the original level of carrier mobility in the Col_h mesophase for both C10PcH₂ and C10PcZn.

component form Col_h mesophase, while the purification of molecularly stacked columns is proceeding on repetitive heating and cooling operations. As depicted in Fig. 6, freshly prepared blends by removing the solvent that would have columns where two discogens are mixed tend to stabilize to be a Col_h mesophase in which two types of single-component columns, one of which is made by C10PcH₂ and another by C10PcZn, form a hexagonal arrangement. 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 form Col_h mesophase and those play a certain role as a electronic hopping path for both hole and electron.

These results may provide a possibility to utilize “miscibility of columnar mesophases” toward the better performance of bulk heterojunction-type organic solar cells by way of the better light harvesting realized by molecular blending of liquid crystalline semiconductors.

3.3 Miscibility of C10PcH₂ and C10PcZn with PCBM

Fig. 9 shows preliminary results of studies on the phase transition behavior of C10PcH₂ / PCBM and C10PcZn / PCBM binary systems. In both cases, one sees the similar trend of miscibility. As the amount of PCBM increases, the clearing point of Col_h mesophase decreases. This means the addition of PCBM leads to destabilization of Col_h mesophase. However, the clearing point gets steady for the additional PCBM amount than 10 mole%, indicating that PCBM is resolved into the Col_h mesophase of C10PcH₂ and C10PcZn up to 10 mole% and the excess amount of PCBM is phase-separated to generate small particles of PCBM in the Col_h phase. It was observed that the PCBM particles are fused into the isotropic liquid phase of Pc mesogens at the higher temperature. The elongation of alkyl chains may lead to the less miscibility of PCBM into the Col mesophase.

In the case of C6PcH₂ / PCBM system, thermal stability of columnar mesophase decreases as the PCBM amount is increased to show a disappearance of Col phase at 20-25 mole% of PCBM and at the component ratio, the observed mobility (hole) shows the maximum that is over the carrier mobility of C10PcH₂ and by C10PcZn.^[14] Interdigitation of linear chains of PCBM is expected to co-exist in the Col mesophase formed by Pc mesogens, though more than 25 mole% of PCBM is stoichiometrically necessary to align along the columnar axis to make a charge hopping path. It is also important to know the factors affect the miscibility of PCBM into discotic columnar arrays in mesophase in order to give an inspiration for the interdigitated p-n heterojunction in a BHJ active layer in OPV studies.

4. SUMMARY

Two mesogenic Pcs, C10PcH₂ and C10PcZn exhibit a complete miscibility in the Col_h mesophase. The hole and electron mobilities of the Col_h mesophase for the 1:1 blend are reduced to the order of 10⁻² cm² V⁻¹ s⁻¹ though those of the pure

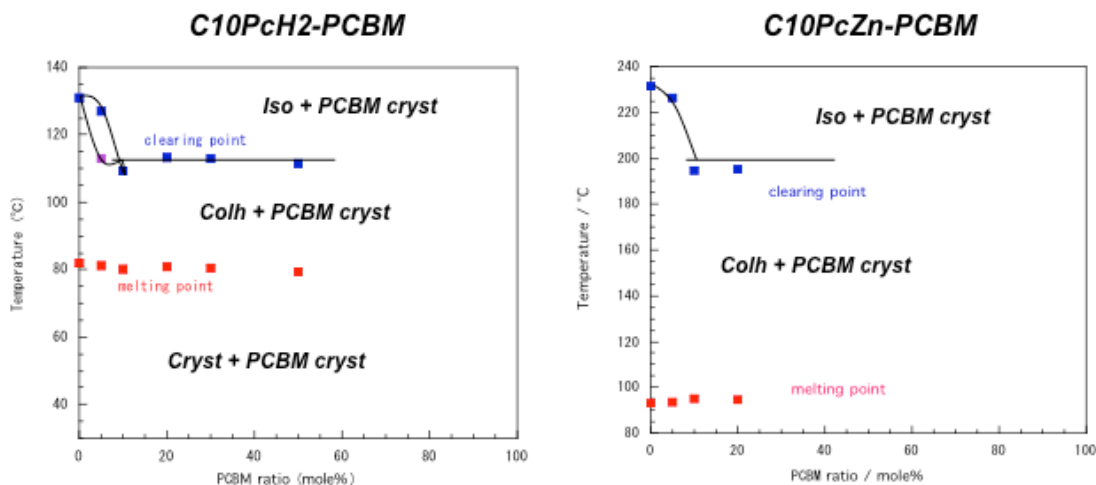


FIGURE 9 : Binary phase diagrams of C10PcH₂ / PCBM and C10PcZn / PCBM systems.

compounds are in the order of $10^{-1} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. However, the repetitive heating and cooling treatment of the binary systems could lead to the recovering of mobility to the original level. These results indicate that the blend of C10PcH₂ and C10PcZn exhibits a Col_h mesophase in which the single component columns of C10PcH₂ and C10PcZn coexist independently to make efficient paths for charge transport. Miscibility of LCs may provide a new tool for the better light-harvesting properties in OPV studies in which electronic transport also can be efficient. Also an importance to know the factors affecting miscibility of PCBM into Col mesophase of Pc mesogens is enhanced for making the better charge transport path as well as the more efficient p/n heterojunction in the system. Miscibility for LC materials may have a glance to a future technology in organic electronics.^[15] Further studies are now under progress.

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