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Author(s)	Miyake, Y.; Hori, T.; Yoshida, H. et al.
Citation	Proceedings of SPIE - the International Society for Optical Engineering. 2011, 7955, p. 795505-1-795505-8
Version Type	VoR
URL	https://hdl.handle.net/11094/75930
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Invited Paper

Liquid Crystalline Phthalocyanines as a Self-Assembling Organic Semiconductor for Solution-Processing Thin Film Devices

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ABSTRACT

A liquid crystalline phthalocyanine semiconductor, 1, 4, 8, 11, 15, 18, 22, 25-hexahexylphthalocyanine ($C6PcH_2$) was studied on the drift mobility of charged carriers by a Time-Of-Flight (TOF) method. It was found that this compound exhibits an ambipolar nature for charge transport and the hole and electron mobilities were determined to be in the order of 10^{-1} cm^2 V^{-1} s^{-1} for polydomain films of the hexagonal disordered columnar (Col_{hd}) mesophase. This is comparable to that of the octyl homologue ($C8PcH_2$) reported by Hanna et al. However, $C6PcH_2$ did not show any tendency to form the homeotropic alignment between ITO-coated glass substrates, though $C8PcH_2$ so clearly and easily does. Clear decay curves of the transient photocurrents could be obtained in TOF measurements even for polydomain films of the crystalline solid phase to give a strongly temperature-dependent mobility of holes which reaches to 1.1 cm^2 V^{-1} s^{-1} at room temperature (RT) as the temperature goes down, whilst the electron mobility slightly increases to be 0.5 cm^2 V^{-1} s^{-1} at RT. This compound could easily form thin films by spin-coating technique with the toluene solution and a simple bulk-heterojunction thin film solar cell was fabricated to give a good performance such as 3.1 % of power conversion efficiency and > 70 % of external quantum efficiency.

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

1. INTRODUCTION

Organic electronics is nowadays one of the most interesting and important research fields for ubiquitous electronic devices with much expectation that it could realize light-weight and flexible electronic devices. 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 in the solvent evaporation to form a film on substrate as well as the fast carrier mobility. Therefore, a self-assembling nature of molecules should be a profoundly related and attractive property for that type of organic semiconductors. This background has made it so interesting to study "organic semiconductors with mesogenicity" because all these requirements are in fact, facilitated properties in liquid crystalline materials. The discovery of fast carrier mobility in mesophase comparable to that of a-silicon (> 10^{-1} cm^2 V^{-1} s^{-1}) [4] where the molecules, more or less, are mobile and/or being fluctuated as a dynamic state of matter, have cast a great impact to the research field of liquid crystals to give "liquid crystalline semiconductor" or "mesophase semiconductor" [5]. However, such dynamic state of molecularly ordered materials have never led to the faster mobility than those of poly-crystalline and single crystalline thin films of organics such as pentacene [6], rubrene [7] and diphenylanthracene [8], though these show the far lower solubility into organic solvents.

On the other hand, it is well-known that the typical molecular shapes of mesogens are of "rod-like (calamitic) and "disc-like"(discotic) and then, the smectic layered and molecularly stacked columnar structures are essentially important

Emerging Liquid Crystal Technologies VI, edited by Liang-Chy Chien, Hiroshi Yokoyama,
Proc. of SPIE Vol. 7955, 795505 · © 2011 SPIE · CCC code: 0277-786X/11/$18 · doi: 10.1117/12.873717

orderings of molecules, respectively, as charge transport materials by an electronic process. In particular, columnar structure is the similar motif to quasi-one-dimentional conductors of arenes and metal complexes [9] in which charges on molecules are likely to transport along the axis of stacking molecules. This is essentially good for electronic hopping process for disordered states of matter, even though the disordered molecular systems are made with an anisotropic order in the aggregation. Therefore, this is well understood in a theoretical aspect described by classical Marcus theory of charge transfer [10], meaning the single process of charge transport is an electronic charge transfer between two molecules and the hopping rate, *k* is described as a following equation,

$$k = (4\pi^2/h)\tau^2(4\pi\lambda k_B T)^{-0.5} \exp(-\lambda/4k_B T) \qquad \text{(Eq.1)}$$

where τ, λ, h, k_B and T are the transfer integral, reorganization energy, Planck constant, Boltzmann constant and temperature, respectively. The transfer integral is a function of interactions between HOMOs of the molecules for hole and LUMOs for electron transports, respectively [11]. The transfer integral, thus, is an important factor for charged carrier mobility in molecular aggregations and a certain length of successive hopping of electron is necessary for high charged carrier mobility as a macroscopic property, which have to be formed in the time scale of pico to nano second order because the time scale of charge hopping between two molecules takes place in the pico second order. This implies that molecular fluctuations in mesophase, more or less, directly relate to the charge hopping efficiency and in the case of the discotic liquid crystalline semiconductors, the molecular displacement to the lateral direction for the columnar axis and a conformational distribution around the columnar axis by rotational fluctuations are crucial for the effective charge hopping along the columnar axis as well as the periodic distance of molecular stacks [12]. Therefore, the dynamic aspects of mesophase should be considered for more efficient charge transport in mesophase and it could be controlled by way of modification of intermolecular interactions in the attractive and repulsive points of view to attain the higher mobility of charged carriers [13].

Recently, Iino et al. found that 1, 4, 8, 11, 15, 18, 22, 25-octaoctylphthalocyanine ($C8PcH_2$) exhibits an ambipolar nature for the mobility in the hexagonal disordered columnar (Col_{hd}) mesophase, while phthalocyanine (Pc) is recognized as a p-type semiconductor [14]. Also the mobilities are rather fast in the order of 10^{-1} cm^2 V^{-1} s^{-1}, exhibiting field-independent property and a slight or non-dependency on temperature which are of typical for liquid crystalline semiconductors [15].

When one sees the history of studies on liquid crystalline Pcs, two types of mesogens could be recognized as a discotic mesogen and those are depicted in Fig.1. It is quite interesting to see that such a fast mobility is obtained for the type B Pc, which is at least comparable to those of the type A. In addition, one can see a contrast between the Type A

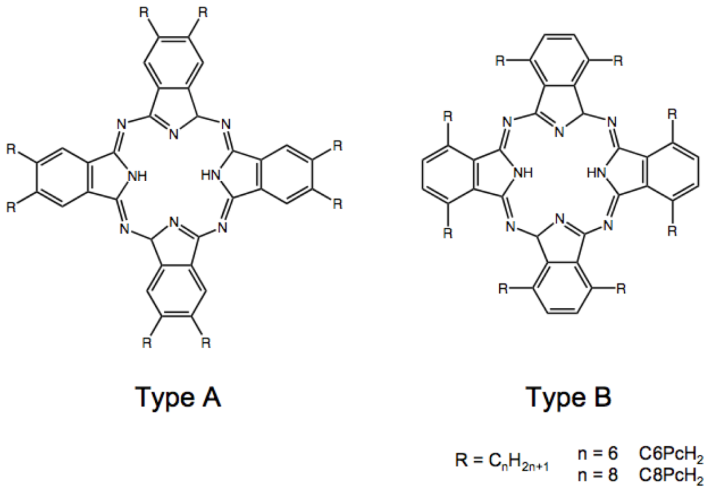

Figure 1: Two types of phthalocyanine discotic liquid crystals. Type A is a derivative of which alkyl or alkoxy chains attach to the 2, 3, 9, 10, 16, 17, 23 and 24 positions of phthalocyanine ring and Type B is a derivative with alkyl chains attached at the 1, 4, 8, 11, 15, 18, 22 and 25 ones.

and B Pcs for the mobilities measured by a Time-Of-Flight (TOF) [16] and Pulse-Radiolysis Time-Resolved Microwave (PR-TRMC) [17] techniques, which could determine the drift and intrinsic mobilities to be 2.6 x 10^{-3} cm^2 V^{-1} s^{-1} and 0.2 cm^2 V^{-1} s^{-1}, respectively.

Considering that the much more bulkiness of alkyl chains in $C8PcH_2$ is derived from the attaching positions of alkyl chains to a Pc ring, it is reasonable to imagine that a steric repulsive interaction arises against the tight stacking of molecules when they form a columnar structure. In fact, the XRD patterns of Col_h mesophase never show the correspondent reflection at 20-28 ° (3.3-3.6 Å), indicating a disordered column [18] and the Col_{hd} mesophase of the type A Pc homologues exhibits the higher thermal stability than those of the type B homologues [19].

In this communication, the surprising results on the carrier mobility of the hexyl homologue ($C6PcH_2$) are shown where the drift mobilities of hole and electron exhibit to be higher to 0.3 -0.4 cm^2 V^{-1} s^{-1}, and these could be determined even in the crystalline phase to be in 10^{-1} ~ 1.4 cm^2 V^{-1} s^{-1} for hole and 0.5 cm^2 V^{-1} s^{-1} for electron. The mesomorphism of $C6PcH_2$ was already reported to exhibit only one mesophase assigned to be of a Col_{hd} type [20].

2. EXPERIMENTAL

2.1 Synthesis and purification of the compound

The compound was synthesized according to the literature with slight modifications as shown in Fig. 2 [20] and fully purified by column chromatography (Silica-gel with toluene as eluent) followed by the repetitive recrystallization from toluene - methanol (1:2) solution.

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 measurements in the temperature range of the mesophase using a Rigaku RINT 2500 HF 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.3. The cell is of sandwich-type consisting of two ITO-coated glass plates as the electrodes (effective area of the electrode : 5 x 5 mm^2) 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

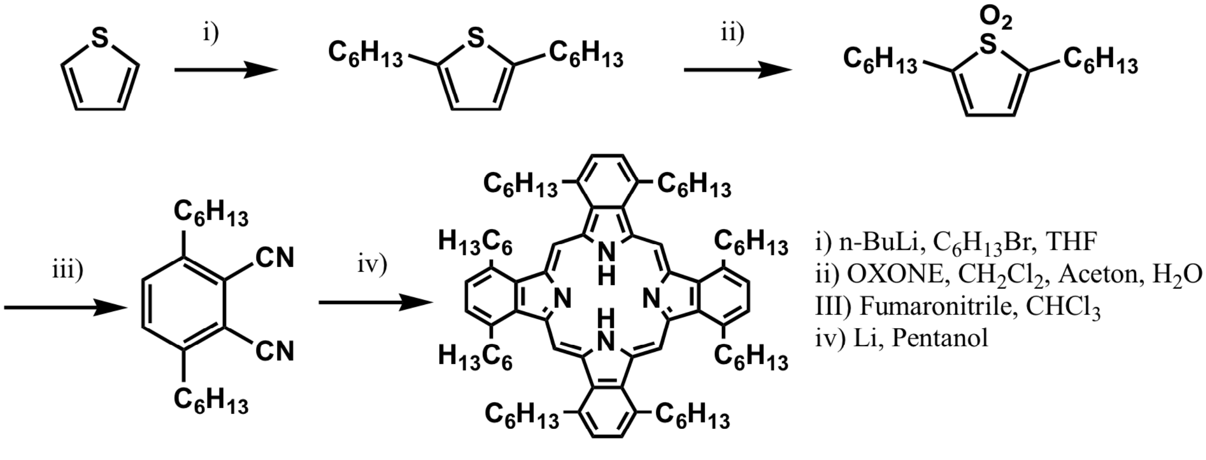

Figure 2: Synthetic route of $C6PcH_2$. [20] Purifications of the final product are so important to obtain clear decay curves of the transient photocurrent in TOF measurements and the reproducibility.

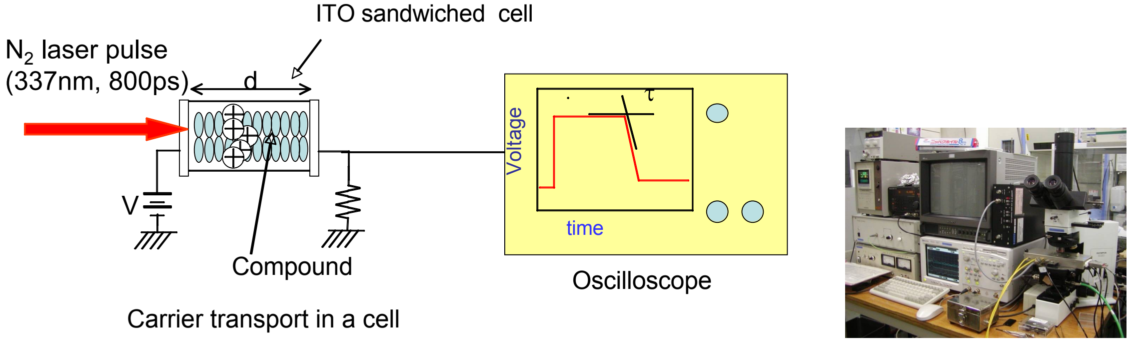

Figure 3 : A schematic drawing of Time-Of-Flight (TOF) apparatus equipped with a polarized microscope.

isotropisation one. A N_2-pulsed laser (337 nm, 800 ps) was used for the photocarrier generation. The DC bias was applied by batteries. 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, μ was calculated by the equation below,

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

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

3. RESULTS AND DISCUSSION

3.1 Mesomorphism

Fig. 4 shows the DSC curves and XRD patterns of the Col_h mesophase for $C6PcH_2$ as the essential properties as a mesophase material. This compound exhibits two endo- and exo-thermic peaks on both heating and cooling runs, meaning that the phase transitions of clearing and melting are of enantiotropic. The crystal-mesophase phase transition takes place at 161 °C and the clearing is seen at 170 °C. An additional phase transition of crystal-crystal is observed at -25 °C. The XRD patterns at 165 °C confirm that the mesophase is assigned to be a Col_{hd} mesophase with a series of reflection peaks of which d-spacings are in the ratio of 1: $1/\sqrt{3}$: 1/2 (d_{10}, d_{11} and d_{20} of the hexagonal arrays of columns) accompanied with only a broad halo at around 2θ = 20 ° (ca. 4.5 A) derived from the molten alkyl chains. The calculated lattice parameter, *a* for the Col_{hd} mesophase is determined to be 20.9 Å (162 °C) and this is a reasonable value for the estimated diameter of molecule (ca. 26 Å with full-extended chains). These results are not incoincident with the published results by Cook et al. [18]

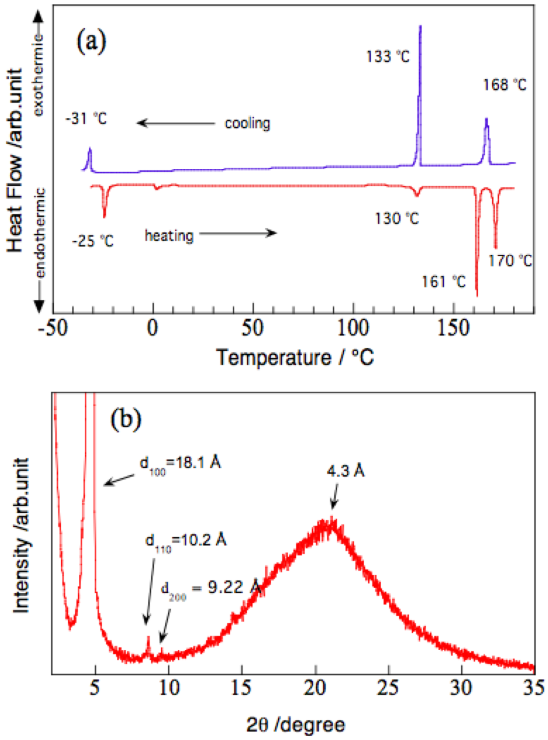

Figure 4: Results of DSC and XRD measurements for $C6PcH_2$. (a) DSC curves (heating and cooling rates : 5 ° C min^{-1}). (b) an XRD pattern for the non-aligned sample at 160 °C.

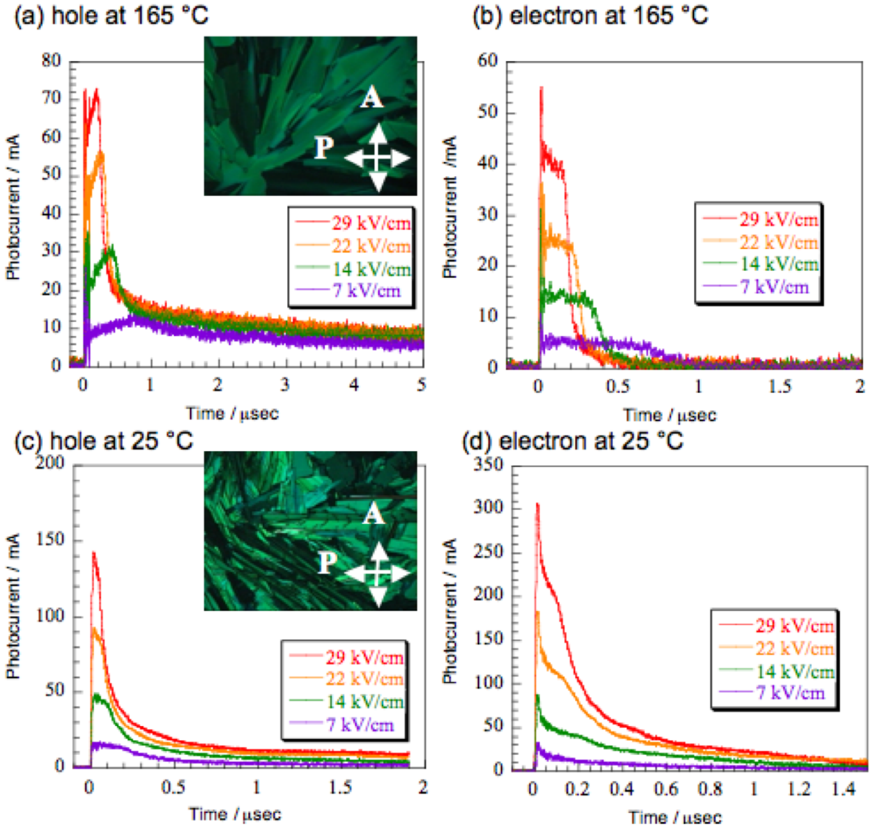

Figure 5: Transient photocurrent decay curves of C6PcH$_2$ in Col$_{hd}$ mesophase (160 °C) for (a) hole and (b) electron and in the solid at 25 °C for (c) hole and (d) electron. Optical textures observed for the cell under a crossed polarizers are shown for both phases.

3.2 Carrier mobility

Fig. 5 shows a typical decay curve of transient photocurrent (hole and electron) for the Col$_{hd}$ and crystalline phases and the optical textures of the cell used for the mobility measurements. Being so different from the spontaneous alignment behaviour of C8PcH$_2$ that exhibits a strong tendency to form a homeotropic alignment (a face-on alignment to the substrate surface) for the Col$_{hd}$ phase, any homeotropic domains was not observed in the poly-domain textures. Nevertheless, very clear decay curves were observed for both hole and electron transports, though the worse situation of decay curves could be recognized for the hole. The mobility is not dependent on the applied field in the range of 7 ~ 29 kV cm^{-1}. An ambipolar nature was evidenced also in C6PcH$_2$ as the C8PcH$_2$ homologue exhibits.

In the Col$_{hd}$ phase, the observed mobility is 0. 2 ~ 0.3 cm^2 V^{-1} s^{-1} as shown in Fig. 6 and mostly of temperature independent and interestingly, the hole mobility is lower than the electronic one. This is the opposite to the result for C8PcH$_2$. On cooling step (the decay curves were measured at the steady state of temperature), the decay curves observed in the temperature range of crystal surprisingly exhibit quite clear ones by which one can easily determined the transit times, even though the optical texture is of poly-domain. As far as we have experienced for a variety of mesophase semiconductors, the crystallization of mesophase gives a poly-domain film to get the decay curves dispersive and consequently it is difficult to determine the transit time, even if a mono-domain state is observed for the mesophase by a polarized microscope.

For the crystalline phase, the hole mobility increases to 1.4 cm^2 V^{-1} s^{-1} from 0.4 cm^2 V^{-1} s^{-1}, as the temperature goes down to -15 °C from 140 °C, while the electron mobility is in almost steady level of 0.4 cm^2 V^{-1} s^{-1} in the same temperature range. The hole mobility is larger than electron one in the crystalline solid phase and the temperature dependence is not similar to each. These features of mobility behaviour were not reported for C8PcH$_2$ and this indicates

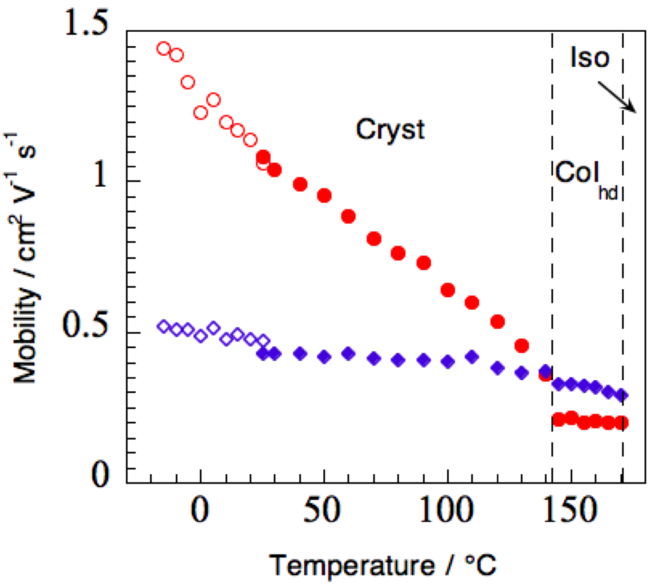

Figure 6 : Temperature dependence of hole (circle) and electron (square) mobilities of C6PcH_2. Filled and open symbols are for the measurements on cooling and heating steps, respectively. The measurements were carried out at the steady state of temperature.

that the crystallization process on cooling from the molten state is different in these two homologues. In additon, optical texture formation of the Col_{hd} phase exhibits something strange [21], indicating that this Col_{hd} mesophase is not of a non-tilted columnar phase with optical uniaxiality, like rectangular columnar mesophase, as Col_h mesophase is optically uniaxial [22].

The hole and electron mobilities in the Col_{hd} mesophase are comparable to those of C8PcH_2. This would be a reasonable, considering the similarity in molecular order for both Col_{hd} mesophases as inferred from the XRD patterns for a non-aligned samples. On the other hand, the single crystal XRD studies were carried out for C6PcH_2 in the early days of chemical studies on this type of mesogenic Pc to show an extraordinary situation for the stacking manner of molecules [23], where one can see a far long distance (8 ~ 9 Å) for the periodical stacking along the *c* axis. On this point of view, the fact that such a fast mobility of charged carriers is observed for the crystalline phase is so strange. However, the Pc planes are possibly so close to each for contacting at the edge of Pc rings. In fact, one can see the overlapping of benzo ring along the *a*-axis. This indicates that in the case of C6PcH_2, the intercolumnar distance in the Col_{hd} mesophase is rather short to a well-defined orientation of columns due to the position of alkyl-attaching site in addition to the shorter chains. In fact, the important feature in XRD results for the Col_{hd} mesophse of C6PcH_2 is that the corresponding Pc derivative of type A which alkyl chains attach at the 2, 3, 9, 10, 16, 17, 23 and 24 sites of a Pc ring exhibits a slightly larger lattice parameter *a* (22.5 Å) probably due to the typical positions as the peripheral part of central core.[19] The shorter intercolumnar distance in the Col_h mesophase of C6PcH_2 would be better for the subsequent charge transport in the lateral direction to the columnar axis.

4. CONCLUSION

It was found that C6PcH_2 exhibit fast mobility with ambipolar carrier transport in both Col_{hd} mesophase and crystalline solid phase to be in the order of 10^{-1} cm^2 V^{-1} s^{-1} and of 10^{-1} to 1.4 cm^2 V^{-1} s^{-1}, respectively. These could be obtained for poly-domain film where the molecules are aligned not in the homeotropic way for the mesophase. These results may imply it is possible to have a novel design concept of liquid crystalline semiconductors which could have efficient charge transport not only along the columnar axis, but also not along it for discotics. Also considering the characteristic properties of Pcs as practical pigments and dyes, $C6PcH_2$ is a good candidature as a solution-processable organic semiconductor for the practical use. Recent results for a simple bulk-heterojunction cell with $C6PcH_2$ and PCBM exhibits a fantastic performance of 3.1 % for the power conversion efficiency with > 70 % for the external quantum efficiency at the Q-band [24] and this also may indicate the peculiarity of $C6PcH_2$ as organic semiconductors.

ACKNOWLEDGMENTS

This study was carried out by a financial support, in part by Grants-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan, the Japan Society for the Promotion of Science (JSPS) Bilateral Joint Projects (Japan - China) and Osaka University Frontier Research Center and the 8 Global Center of Excellence (Global COE) Program "Center for Electronic Devices Innovation" at Osaka University.

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