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Hirosato Monobe^a, Yo Shimizu^a, Shuichi Okamoto^a
& Hiroyuki Enomoto^b

^a Nanotechnology Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Ikeda, Osaka, Japan

^b Osaka Electro-Communication University, Hatsumachi, Neyagawa, Osaka, Japan

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Hirosato Monobe
Yo Shimizu

Nanotechnology Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Ikeda, Osaka, Japan

Shuichi Okamoto

Nanotechnology Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Ikeda, Japan;
Osaka Electro-Communication University, Hatsumachi, Neyagawa, Osaka, Japan

Hiroyuki Enomoto

Osaka Electro-Communication University, Hatsumachi, Neyagawa, Osaka, Japan

In this study, ambipolar charge carrier transport properties were investigated for a homologous series of triphenylene by time-of-flight (TOF) technique for the homeotropic domains. Ambipolar electronic charge carrier transport was observed and the both positive and negative charge carrier mobilities decrease with the increase of the alkyl chain length. Ionic conduction was also observed for the negative charge carrier transport except for C4OTP and any remarkable dependency of the alkyl chain length was not seen. It was reasonably found that both the positive and negative charged carrier mobilities by electronic hopping process is affected by the intra columnar order.

Keywords: ambipolar; charge carrier transport; columnar; triphenylene

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Address correspondence to Hirosato Monobe, Nanotechnology Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), 1-8-31 Midorigaoka, Ikeda, Osaka, 563-8577, Japan. E-mail: monobe@ni.aist.go.jp

INTRODUCTION

Columnar liquid crystals of discotics have been drawing much attention as novel organic semiconductors due to the fast charge transport phenomena along a columnar axis [1–12] as well as the anisotropic property of conduction along the columns [13] in the recent decade. In fact, in highly ordered columnar mesophases, fast carrier mobility ($\sim 10^{-1} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) by electronic process of carrier transport was found which is comparable to those of amorphous silicon [2,5,9,10]. And, thus, the applications as one-dimensional conductors, photoconductors, molecular wires and fibers, light emitting diodes and photovoltaic cells have also been exploited. Thereafter, a series of reinvestigations of rod-like liquid crystals have also revealed their good performance as a semiconductor with a fast mobility ($\sim 10^{-1} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) in highly ordered smectic phases [14–16]. Furthermore, columnar liquid crystals are expected as a self-organized molecular semiconductor to fabricate the related devices by solution process. In addition, the ambipolar charge carrier transport is another important property as the organic semiconductors [10–12]. Liquid crystalline semiconductors are very effective in improving the present device with their unique features of electrically inactive structural defects including domain boundaries and high ambipolar mobility. Recent studies of columnar liquid crystal semiconductors indicate the electronic transport in columnar mesophase could strongly depend on the dimension of columnar order [3,6,11,12]. However, there are no detailed study of charge carrier transport properties in the same columnar mesophase with different alkyl chain length. It might be interested in carrier transport phenomena in the similar structure of π -stacking with different substitution for columnar liquid crystals.

In this work, ambipolar charge carrier transport properties were investigated for a homologous series of 2,3,6,7,10,11-hexaalkyloxytriphenylene (CnOTP; $n = 4-8$, alkyl chain length) by time-of-flight (TOF) technique for the homeotropic domains. Temperature dependence of positive and negative charge carrier mobilities were also reported for Col_h and Col_{hp} mesophases dependent on the alkyl chain length.

EXPERIMENTAL

^1H -NMR spectra were recorded on a JEOL JNM-Alpha 500 MHz spectrometer using Me_4Si as an internal standard. The phase transition temperatures and enthalpies were detected by a Differential Scanning Calorimeter (TA Instrument, 2920 MDSC) and the textures of the mesophases were observed by a polarizing microscope (Olympus, BH-2) equipped with a hot stage (Mettler, FP80HT).

Powder X-ray diffraction studies were carried out by using a Rigaku Geigerflex X-ray diffractometer (CuK α) with a custom hotstage. The charge carrier mobilities were measured by TOF method on a liquid crystal film sandwiched between ITO covered glass plates. The cell was capillary filled in under an inert gas (Ar) after being degassed under vacuum. By slowly cooling the sample from the isotropic state, the sample showed a spontaneous homeotropic texture in a certain area. 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 N₂ laser ($\lambda = 337$ nm, 800 ps, $\phi = 1$ mm) was used for a pulsed light irradiation. A transient photocurrent was detected by a digital oscilloscope (Hewlett Packard, HP54820A) with a handmade preamplifier.

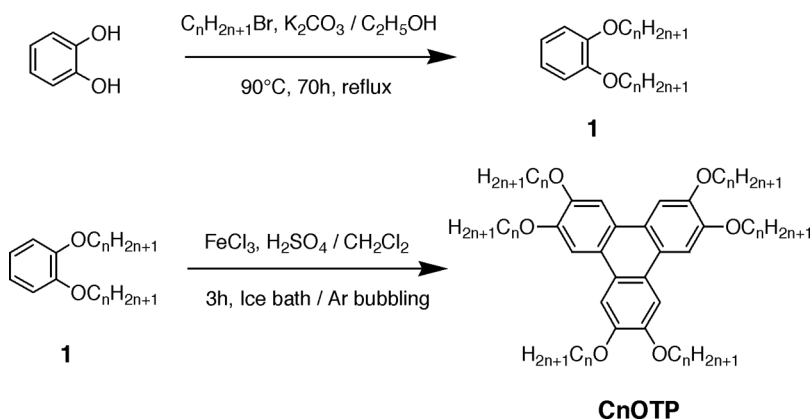
Compounds

The synthesis of compounds were carried out according to the literatures with slight modifications [17,18]. Alkylation of 1,2-dihydroxybenzen and the following cyclization reaction of the resultant 1,2-dialkoxybenzen with FeCl₃ gave the homologous series of CnOTPs. The synthetic route is illustrated in Scheme 1.

1,2-dialkoxybenzene (1)

The compounds were synthesized by the same method except for alkyl chain length of alkylbromide. The synthetic procedure of 1,2-dipentyloxybenzene ($n = 5$) is described below.

1-Bromopentane (15.7 g, 0.10 mol) was slowly added into the ethanol solution of 1,2-dihydroxybenzene (4.8 g, 0.043 mol) and K₂CO₃



SCHEME 1 Synthetic route of 2,3,6,7,10,11-hexaalkoxytriphenylene (CnOTP).

(28.9 g, 0.21 mol) with vigorous stirring. The reaction mixture was stirred under reflux for 96 h and filtered using celite after cooling. The solvent was evaporated *in vacuo*. The crude product was purified by column chromatography (silica gel; dichloromethane : hexane = 1:1, R_f = 0.66) to give 1,2-dipentyloxybenzen (8.6 g, 0.034 mol 79%) as colorless liquid.

(**n** = 4)

¹H-NMR (CDCl₃) δppm: 6.89 (s, 4H, ArH), 4.00 (t, 4H, OCH₂) 1.80 (m, 4H, OCH₂CH₂), 1.51 (m, 4H, CH₂CH₃), 0.98 (t, 6H, CH₃).

(**n** = 5)

¹H-NMR (CDCl₃) δppm: 6.88 (s, 4H, ArH), 3.99 (t, 4H, OCH₂) 1.82 (m, 4H, OCH₂CH₂), 1.34 (m, 8H, (CH₂)₂CH₃), 0.93 (t, 6H, CH₃).

(**n** = 6)

¹H-NMR (CDCl₃) δppm: 6.89 (s, 4H, ArH), 3.99 (t, 4H, OCH₂), 1.81 (m, 4H, OCH₂CH₂), 1.47 (m, 4H, O(CH₂)₂CH₂), 1.34 (m, 8H, (CH₂)₂CH₃), 0.90 (t, 6H, CH₃).

(**n** = 7)

¹H-NMR (CDCl₃) δppm: 6.88 (s, 4H, ArH), 3.99 (t, 4H, OCH₂), 1.81 (m, 4H, OCH₂CH₂), 1.48 (m, 4H, O(CH₂)₂CH₂), 1.32 (m, 12H, (CH₂)₃CH₃), 0.89 (t, 6H, CH₃).

(**n** = 8)

¹H-NMR (CDCl₃) δppm: 6.89 (s, 4H, ArH), 3.99 (t, 4H, OCH₂), 1.81 (m, 4H, OCH₂CH₂), 1.47 (m, 4H, O(CH₂)₂CH₂), 1.34 (m, 16H, (CH₂)₄CH₃), 0.88 (t, 6H, CH₃).

2,3,6,7,10,11-Hexaalkyloxytriphenylene (CnOTP)

The compounds were synthesized by the same method using a correspond alkyl chain length of 1,2-dialkyloxybenzene. The synthetic procedure of 2,3,6,7,10,11-hexapentyloxytriphenylene (C5OTP, n = 5) is described below.

Anhydrous iron (III) chloride (6.0 g, 0.037 mmol) and sulfuric acid (5 drops) were added to a mixture of 1,2-dipentyloxybenzene (2.42 g, 9.7 mmol) in dichloromethane (150 mL) with vigorous stirring in the ice bath. When the reaction was stirred for 3 hours, approximate 130 mL methanol was slowly add to the mixture. The solvent was evaporated *in vacuo*. The resultant precipitate was filtered off. The crude product was purified by column chromatography (silica gel; hexane: ethylacetate = 1:20, R_f = 0.17) and further purification by recrystallization from the mixture of ethanol and hexane to give C5OTP (1.04 g, 1.38 mmol, 43%) as white solid.

(**n** = 4)

¹H-NMR (CDCl₃) δppm: 7.84 (s, 6H, ArH), 4.24 (t, 12H, OCH₂), 1.93 (m, 12H, OCH₂CH₂), 1.61 (m, 12H, CH₂CH₃), 1.04 (t, 18H, CH₃).

(**n** = 5)

¹H-NMR (CDCl₃) δppm: 7.84 (s, 6H, ArH), 4.23 (t, 12H, OCH₂), 1.58 (m, 12H, OCH₂CH₂), 1.45 (m, 24H, (CH₂)₂CH₃), 0.98 (t, 18H, CH₃).

(**n** = 6)

¹H-NMR (CDCl₃) δppm: 7.83 (s, 6H, ArH), 4.23 (t, 12H, OCH₂), 1.94 (m, 12H, OCH₂CH₂), 1.58 (m, 12H, O(CH₂)₂CH₂), 1.40 (m, 24H, (CH₂)₂CH₃), 0.93 (t, 18H, CH₃).

(**n** = 7)

¹H-NMR (CDCl₃) δppm: 7.83 (s, 6H, ArH), 4.23 (t, 12H, OCH₂), 1.94 (m, 12H, OCH₂CH₂), 1.55 (m, 12H, O(CH₂)₂CH₂), 1.33 (m, 36H, (CH₂)₃CH₃), 0.91 (t, 18H, CH₃).

(**n** = 8)

¹H-NMR (CDCl₃) δppm: 7.83 (s, 6H, ArH), 4.23 (t, 12H, OCH₂), 1.94 (m, 12H, OCH₂CH₂), 1.57 (m, 12H, O(CH₂)₂CH₂), 1.32 (m, 48H, (CH₂)₄CH₃), 0.90 (t, 18H, CH₃).

RESULTS AND DISCUSSIONS

Phase Transition Behaviors

CnOTPs show some endothermic peaks on heating corresponding to the crystal to crystal, crystal to mesophase and the isotropic melt. On cooling process, there are two exothermic peaks corresponding to the isotropic to mesophase and crystal exclusive of C4OTP. C4OTP shows an additional peak on cooling. All homologues exhibited at least an enantiotropic

TABLE 1 Phase Transition Temperature [°C] and Transition Enthalpy [kJ/mol] in Parenthesis from DSC Curves of CnOTPs (Above Table: Experimental Values, Below: Literature Values)

Compound	n	Cr	Col _{hp}		Col _h		Iso	ref
C4OTP	4	•	85.6 [22.8] 88.6	•	143.9 [18.7] 145.6		•	[19]
C5OTP	5	•	70.1 [33.7] 69			• 121.7 [10.8] 122	•	
C6OTP	6	•	66.7 [42.2] 67			• 98.8 [5.8] 99.5	•	[19]
C7OTP	7	•	65.5 [57.7] 68.8			• 91.6 [5.1] 93	•	
C8OTP	8	•	66.6 [108.5] 66.8			• 84.4 [5.5] 85.6	•	[19]

mesophase. The thermodynamic data from DSC measurements of the CnOTPs used in this study are summarized in Table 1 as compared to the those of literatures [17, 19]. The phase transition temperatures of CnOTPs by DSC measurements were corresponded within ca. 2°C.

XRD Analysis

X-ray diffraction measurements for CnOTPs were performed at 95% reduced temperature of clearing temperature (K) in the mesophase. Figure 1 shows the X-ray diffraction patterns of these homologues. These are a typical pattern of XRD for hexagonal columnar (Col_h) mesophase exclusive of C4OTP. A set of reflections corresponding to d_{100} , d_{110} and d_{200} 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. The Additional two reflections were observed at ca. 4.5Å (broad halo) and ca. 3.5Å (weak peak for C6 to C8OTP and sharp peak for C5OTP), which are assigned to the average distance of the molten alkyl chains and intracolumnar order, respectively. Sharp reflections near ca. 3.5Å strongly indicates the ordered columnar phase for C4 and C5OTP, and these are columnar hexagonal plastic (Col_{hp}) and

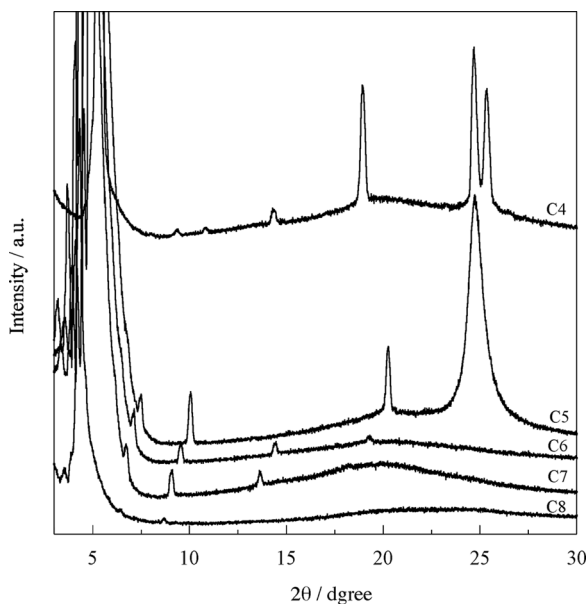


FIGURE 1 Powder XRD patterns of CnOTPs at 95% reduced temperature of clearing point.

TABLE 2 The d-Values [Å] from XRD Results in C_nOTPs. The Measurement Temperature were Equal to 95% of Relative Temperature from Clearing Temperature [K]

Reflection	Compounds				
	C4OTP	C5OTP	C6OTP	C7OTP	C8OTP
(100)	16.47	17.42	18.28	19.49	20.11
(110)	9.41	11.75	12.27	13.00	13.57
(200)	8.18	8.77	9.18	9.77	10.10
(210)	6.17				
(300)			4.61	6.48	
(220), (211)	4.68				
(400)		4.38			
(311), (320)	3.83				
(001)		3.60			
(002)	3.60				
(102)	3.51				

ordered columnar hexagonal (Col_{ho}) mesophases, respectively [3]. On the other hand, C6 to C8OTP show only weak peak corresponding to the intracolumnar order and this suggests those are disordered columnar hexagonal (Col_{hd}) mesophase. The results of XRD measurements are summarized in Table 2. Figure 2 shows the temperature dependence of intracolumnar periodicity for C4 and C5OTP. This indicates the stacking periodicity decreases with decreasing of temperature in

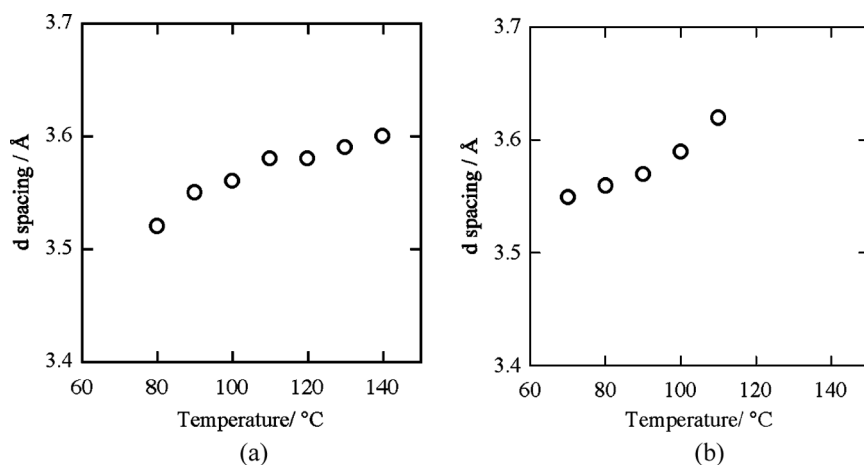


FIGURE 2 Temperature dependence of stacking periodicity for (a) C4OTP and (b) C5OTP.

the mesophase. The textures of mesophase were similar to a typical texture for Col_h mesophase for CnOTPs exclusive of C4OTP which shows highly ordered Col_{hp} mesophase.

Charge Carrier Transport Property

The transient photocurrent measurements have been performed by TOF technique for the homeotropically aligned area to investigate the charge transport along the columnar axis. Figure 3(a) and (b) show a typical transient photocurrent of C6OTP (90°C, thickness 15 μm) for positive and negative carriers in the mesophase under various electric fields, respectively. Figure 4 shows alkyl chain length and temperature dependence of the charge carrier mobilities of CnOTPs for positive and negative carriers. The ambipolar carrier transports were observed for the all of CnOTPs. However, in fact, in order to obtain the ambipolar electronic carrier transport, it was needed careful purification of compound by means of repeated recrystallization. A clear fast transit was observed which corresponded to the transport of positive and negative charge carriers by electronic process and the mobilities of $10^{-4} \sim 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at a short time range of microseconds without electric field dependence. For negative carriers, there existed an additional slow transit at a longer time scale of millisecond as shown in Figure 3(b), which corresponded to ionic conduction and a mobility of $10^{-6} \sim 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ exclusive of C4OTP probably due to its high viscosity. For electronic transport, the charge carrier mobility of C4, C5 and C6OTP depends on the columnar mesophases

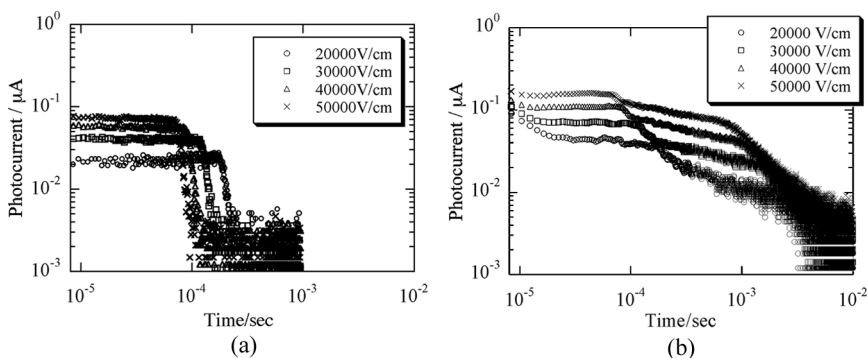


FIGURE 3 Transient photocurrent curves taking by TOF method of C6OTP 15 μm cell at 90°C under various electric field for (a) positive and (b) negative charge carriers.

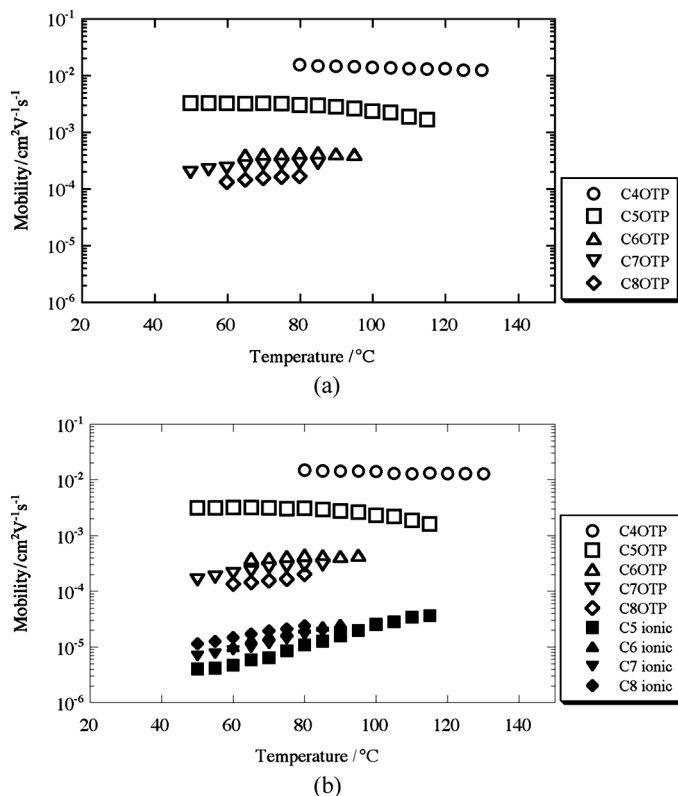


FIGURE 4 Temperature dependence of charge carrier mobilities of CnOTPs for (a) positive and (b) negative charge carriers.

(Col_{hp} , Col_{ho} and Col_{hd} , respectively) according to previous reports [3,6,11,12]. According to the XRD measurements, C4OTP and C5OTP have a high intracolumnar order in the vicinity of 3.5\AA , in contrast to the undetectable intracolumnar order of the longer homologues. It was reasonably found that both the positive and negative charged carrier mobilities by electronic hopping process is affected by the intracolumnar order. On the other hand, the electronic carrier mobilities of C6, C7 and C8OTP in Col_{hd} mesophase decrease with increasing of alkyl chain length although XRD patterns show no difference in the wide angle region which corresponds to the intracolumnar order. It was reasonably found that both the positive and negative charged carrier mobilities by electronic hopping process is affected by the intracolumnar order in the same manner. Temperature dependence of the charge carrier mobility was also seen in Figure 4. For C4 and C5OTP,

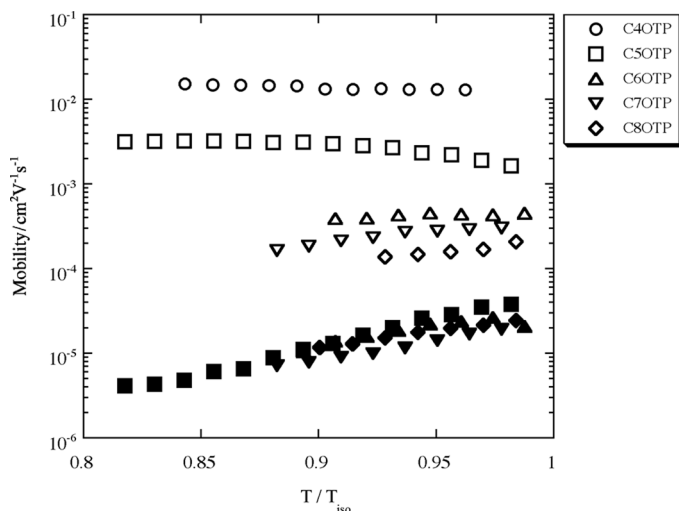


FIGURE 5 The reduced temperature dependency of the negative charge carrier mobility of CnOTPs. The open circles presented for electronic transport and the closed ones indicate for the slower ionic migration.

the electronic carrier mobility were almost constant and slightly increased with decreasing of temperature. These are consistent with the the temperature dependence of intra columnar periodicity as shown in Figure 2. On the contrary, the charge carrier mobility decreases with decreasing of temperature for C6 to C8OTP. This implies that the thermal activation hopping process were the dominant factor for carrier transport in Col_{hd} phase. Figure 5 shows temperature dependence of the slower ionic carrier mobility by using the reduced temperature from the clearing point for CnOTPs exclusive of C4OTP. No dependency of alkyl chain length was observed for the ionic carrier mobility. Consideration of micro-segregation in the mesophase materials, it is very reasonable that the ions migrate to a fluid-like region which consist of substituted alkyl chains aggregating loosely, while the core triphenylene part was stacked rigidly. This implies that there were no significant difference in the state of alkyl side chains in the columnar structure for C6 to C8OTP in spite of those of intracolumnar π -stacking was slightly decrease with increasing of the alkyl chain length.

CONCLUSION

Ambipolar electronic charge carrier transport was observed for CnOTPs and the both positive and negative charge carrier mobilities

decrease with the increase of the alkyl chain length. Ionic conduction was also observed for the negative charge carrier transport exclusive of C4OTP and any remarkable dependency of the alkyl chain length was not seen. It was reasonably found that both the positive and negative charged carrier mobilities by electronic hopping process is affected by the intracolumnar order. The electronic carrier mobilities of C6 to C8OTP decrease with increasing of alkyl chain length in spite of XRD patterns show no difference in the wide angle region with alkyl chain length. These results imply that the intracolumnar order of C6 to C8OTP decreases with increasing of alkyl chain length. It would be possible to estimate the order of intra columns of columnar liquid crystals from its electronic carrier mobility in the mesophase.

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