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Carrier Mobility Behavior of Triphenylene Mesogen with a Hydrogen Bonding Amide Group

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*The charged carrier mobility was measured for the Col_h mesophase of a hexa-substituted triphenylene of which one of the peripheral pentyloxy chains is replaced with n-butylamideethyleneoxy group (**1**) to compare that of hexapentyloxytriphenylene (**2**). The positive charge mobility was observed to be in the order of $10^{-5} \sim 10^{-4}\ cm^2\ V^{-1}\ s^{-1}$. Though the thermal stability of Col_h mesophase is higher than that of **2**, the carrier mobility of **1** is smaller by one order of magnitude probably due to the presence of an electrical dipole of the carbonyl group. Also the temperature dependence of mobility in **1** exhabits a thermally activation behavior in a stronger way than in **2**, indicating the hydrogen bond interaction affect the thermal behavior of charge hopping by a modification of molecular dynamics.*

Keywords Hydrogen bonding; liquid crystalline semiconductor; Time-Of-Flight (TOF); triphenylene

1. Introduction

In the middle of 1990s, high carrier mobility comparable to that of amorphous silicon (in the order of $10^{-1}\,cm^2\,V^{-1}s^{-1}$) was reported for a highly ordered columnar mesophase [1,2]. Similar carrier mobility have been observed for Hexabenzocoronene(HBC) [3] and phthalocyanine(Pc) [4] in not so highly ordered columnar mesophase. The carrier transport mechanism in mesophases is generally explained by a hopping mechanism. From Marcus formalism [5,6], the following Eq. (1) is good

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for the charge hopping rate, k_{ET}

$$k_{ET} = \frac{4\pi^2}{h} t^2 \frac{1}{\sqrt{4\pi\lambda RT}} e^{-\lambda/4RT} \tag{1}$$

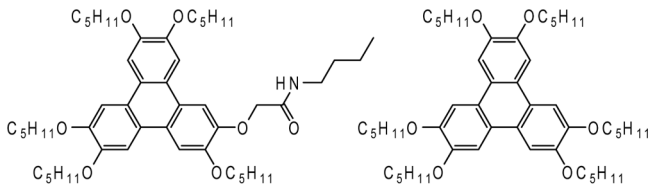
Where t, λ, T, h, and R are transfer integral, reorganization energy, planck constant and gas constant respecting. Therefore, the hopping rate (k_{ET}) strongly depends on the transfer integral (t) which is determined with HOMO and LUMO energy levels of the molecule. Consequently, it is suggested the carrier mobility is not increased by smaller inter-disk distance within a column. Recently, it was reported that the charge conduction in discotic liquid crystals is significantly affected by the rotational configuration of disc-shaped molecules around the columnar axis and the translational disorders off-setting of the discotic molecules in a column [7,8]. Therefore, the fluctuation control of molecules is important strategy for this issue. Recently, Ivanov *et al.* reported that a hexacarboxyamidehexaazatriphenylene mesogen shows the smallest inter-disk distance (3.18 Å). However, the carrier mobility was evaluated to be in the order of $10^{-2}\,cm^2V^{-1}\,s^{-1}$ by Pulse-radiolysis-time-resolved microwave conductive technique [9].

In this work, we measured the carrier mobility of a hexapentyloxy triphenylene of the one alkoxy tail was modified with an alkylamide group (**1**) (Scheme 1) to reveal how one point hydrogen bond site affect the carrier mobility behavior.

2. Experimental

1 was synthesized according to the procedure previously reported [10]. The mesogen **1** shows a Col_h mesophase between 72°C and 152°C as shown in Figure 1. The thermal stability of Col_h phase is enhanced by *ca.* 30°C in the introduction of one hydrogen bond site into the peripheral part of triphenylene, as the corresponding hydrocarbon homologue, **2** has 69°C and 122°C for the melting and clearing points, respectively [11].

The carrier mobility was evaluated by a Time-Of-Flight (TOF) technique. The sample cell for the mobility measurements consists of two ITO-coated glasses separated by polyimide films as a spacer (12.5 μm-thick). The actual cell gap was evaluated by an interferometry technique using a UV-visible spectrometer (Shimazu, UV-2500PC). The cell configuration is depicted in Figure 2. The sample was injected into the cell gap at a temperature of the isotropic phase by capillarity action. A homeotoropic alignment was obtained on gradually cooling from the isotropic



Scheme 1. Chemical structures of **1** and **2**.

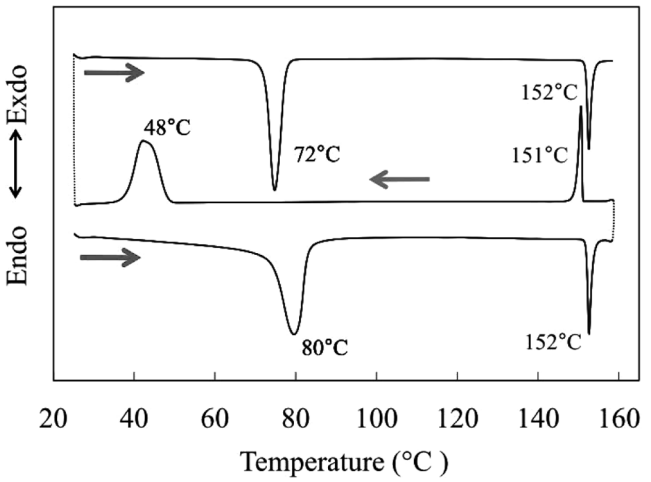


Figure 1. DSC diagram of **1**. Heating and cooling rate: 5°C/min.

phase. Bias voltage was applied across the sample cell and a N_2 pulsed laser was used as the excitation light source (wave length = 337 nm, pulse width = 800 ps). The mobility was calculated by the following equation $\mu = l^2/t_\tau V$ (μ: mobility, l: sample thickness, t_τ: transit time, V: applied voltage). The details of TOF measurement are described elsewhere [12].

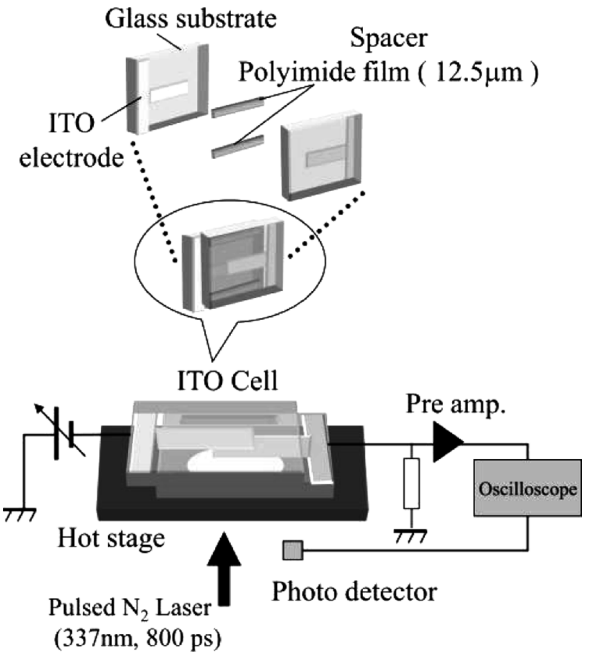


Figure 2. Schematic diagram of the TOF equipments with the cell.

3. Results & Discussion

Figure 3(a) shows transient photocurrent decay curves for the positive carriers in which one can observe well-defined transit-times. The mobility of negative carrier could not be determined because the transient photocurrent decay curves were dispersive. The mobility of positive carrier was calculated to be $3.5 \times 10^{-4}\,cm^2\,V^{-1}\,s^{-1}$ at 145°C which is decreased by one order of magnitude is comparison to that of **2** [13].

The carrier mobility was essentially independent of the applied electric field as shown in Figure 3 and this is a common characteristic for discotic liquid crystalline semiconductors [14] and also the same behavior is observed for **2**. The temperature dependence of carrier mobility for the positive carriers of **1** exhibits thermally activated behavior and two regions of temperature would be recognized for the variant activation energy ($EA = 0.33\,eV$ for $T > ca.$ 90°C and $0.57\,eV$ for $T < ca.$ 90°C) shown in Figure 4. These *Ea* values are comparable to those of ionic transport

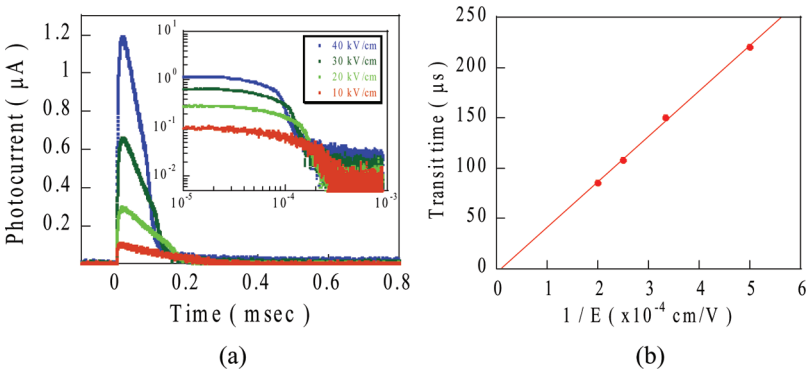


Figure 3. (a) Photocurrent decay curves of the positive carrier and (b) applied field dependence of the carrier mobility for **1** in the Col_h mesophase at 145°C.

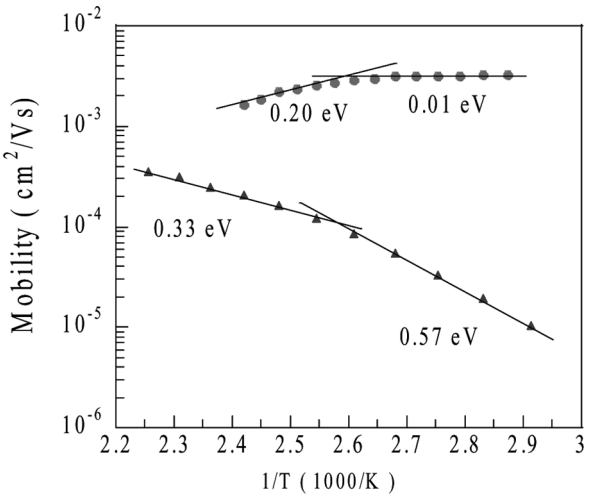


Figure 4. Arrhenius plots of the mobility for the positive charge in **1** (closed triangle) and **2** (closed circle).

Table 1. Phase transition behavior of **1** and **2**

Compound	Phase transitions				
1	Cryst	72°C (34.7 kJ/mol)	Col_h	152°C (8.0 kJ/mol)	Iso
2	Cryst	69°C (32.6 kJ/mol)	Col_h	122°C (8.5 kJ/mol)	Iso

observed for columnar mesophases of discotics [15,16]. On the other hands, the carrier mobility of **2** is almost independent of temperature and the carrier mobility is decreased with the temperature approaching to the isotropization one. This may indicate that **1** has broad distribution of density of state (DOS) of HOMO and LUMO level due to the pining of stacked molecules to each by hydrogen bond interaction.

The carrier mobility of **1** in the Col_h mesophase is smaller than that of **2**. However, the thermal stability of **1** in the Col_h mesophase is higher than that of **2** (Table 1). The powder XRD measurements indicates a slight different in the lattice constant of hexagonal arrange of columns and the stacking periodicity within a column.

The lattice constant of the **1** was calculated to be 20.5 Å is slightly increased for that of **2** (20.1 Å). Two diffused reflections come up at *ca.* 4.3 Å corresponding to the liquid-like order of the aliphatic hydrocarbon chains [17] and the molecular stacking orders of core parts in column were detected at 3.69 Å and at 3.60 Å for **1** and **2**, respectively. The intra columnar periodicity of **1** is slightly increased in comparison to **2**. The low mobility and strong temperature dependence observed for **1** is coincident with the XRD results. However, it was reported the transfer integral is significantly affected by the rotational configuration of molecules around the columnar axis than the stacking periodicity of molecules along the column axis. The staggered configuration (Fig. 6) with minimum value of transfer integral is might be stabilized by due to the pining of stacked molecules to each by hydrogen bond interaction or

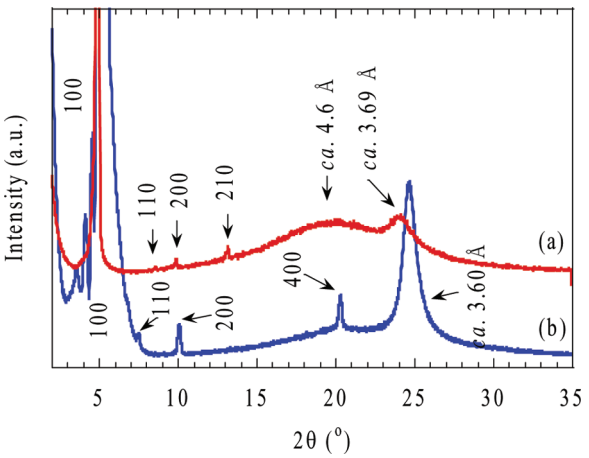


Figure 5. Powder X-Ray diffraction patterns of Col_h mesophases (a) **1** at 144°C and (b) **2** at 110°C ($T/T_{Iso} = 0.95$).

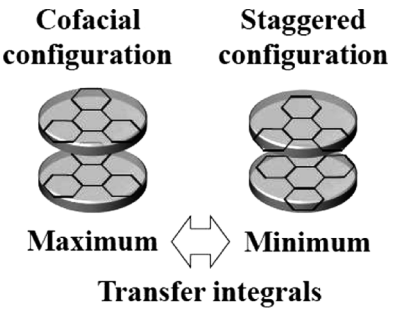


Figure 6. Relationship between stacking configuration and transfer integrals for a discotic liquid crystal.

these behavior of **1** is possibly interpreted on the presence of an electric dipole-carrier interaction [18].

4. Conclusion

The carrier mobility in the Col_h mesophase of **1** was evaluated by TOF measurements. The positive carrier of **1** are in the order of $10^{-5} \sim 10^{-4}\,cm^2\,V^{-1}\,s^{-1}$. The carrier mobility is independent of the applied field ranging from 10 to 40 kV/cm. These carrier transport properties are almost identical to those of **2**.

The XRD measurements indicate that the mesophase of **1** is a hexagonal ordered columnar (Col_{ho}) one, analogous to **2** with a slightly difference in the intra-columnar stacking periodicity, being coincident with the difference of mobility. Further, studies are in program for the bis and trifunctional derivatives of **1**.

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