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Charged Carrier Mobility Study in $\mathbf{Col_h}$ Mesophase of Perfluoroalkylated Triphenylene Derivatives

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The charged carrier mobility was measured for a Col_{hd} *mesophase of a perfuluoroalkylated triphenylene derivative to compare that of the corresponding non-fluorinated alkoxy derivative. The mobility was determined for both positive and negative charges which is in the order of* $10^{-4}\,cm^2V^{-1}s^{-1}$. *In the negative electrode illumination, the transient photocurrent decay carves consist of the fast and slow components and the latter is probably derived from an ionic transport. Though the perfluoroalkylated triphenylene shows the higher thermal stability of a* Col_{hd} *mesophase, than the corresponding hydrogen homolougue, the mobility is in the same order and the ambipolar character is shared.*

Keywords Liquid crystalline semiconductor; Time-Of-Flight (TOF); triphenylene

1. Introduction

In the new era of organic electronics, liquid crystalline semiconductors are one of the interesting and important categories as promising materials in terms of self-assembling organic semiconductors which are derived from dynamic states of molecular aggregations. In particular, the applications to thin film devices are now in the featuring stage of research and developments as "Mesophase Semiconductors" [1].

On the discotic liquid crystalline semiconductors, a requirement for the faster mobility of carriers has been studied in extending the π-electronic conjugation system to get the transfer integral increased [2]. Hexabenzocolonene mesogens are the typical example and the carrier mobility was reported to be in the order of $10^{-1}\,cm^2\,V^{-1}\,s^{-1}$ [3] and of $10^{-2}\,cm^2\,V^{-1}s^{-1}$ [4] in their columnar mesophases by the pulsed

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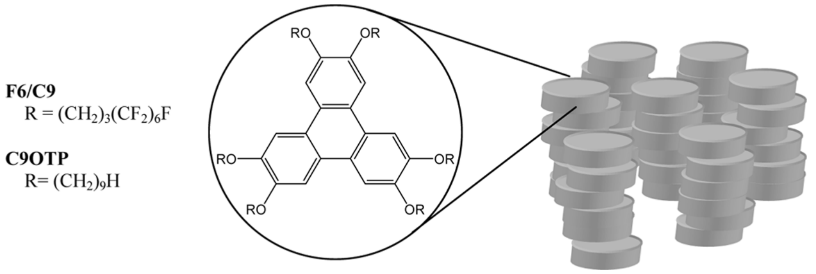


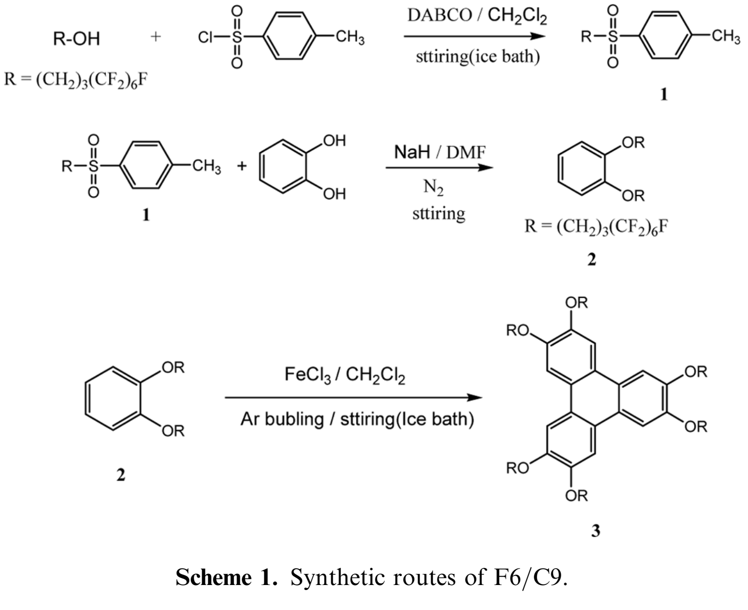
Figure 1. Chemical structure of a perfluoroalkylated triphenylene and the corresponding hydrogen homologue with a schematic view of the molecular order of hexagonal disordered columnar (Col$_{\text{hd}}$) mesophase.

radiolysis time-resolved microwave conductivity (PR-TRMC) [5] and Time-Of-Flight (TOF) [6] techniques, respectively.

A series of alkoxytriphenylenes has been extensively studied so far as a typical liquid crystalline semiconductor [7]. However, the correlation of molecular dynamics to the observed carrier mobility behavior has not been clarified yet. Recently, we reported the mesomorphism of perfluoroalkylated triphenylenes (Fig. 1) in which the columnar mesophase stability (Col$_{\text{hd}}$ mesophase) is enhanced, though the intra-columnar structure is not ordered even for the shorter homologues [8]. In this communication, the carrier mobility determined by a TOF technique for the homeotropic film in the sandwich-type cells is reported.

2. Experimental

A perfluoroalkylated triphenylene (F6/C9) was synthesized as shown in Scheme 1. 1H,1H,2H,2H,3H,3H-perfluorohexane-*p*-toluensulphonate (1) was prepared by



Scheme 1. Synthetic routes of F6/C9.

the tosylation of perfluoroalkyl alcohol [9]. 1,2-Di(1H,1H,2H,2H,3H,3H-perfluorononyloxy)benzene (2) was synthesized as the following procedure.

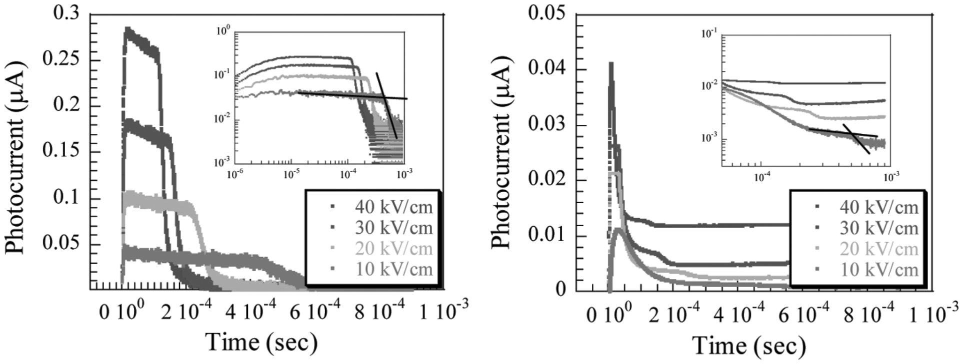
Catechol (0.9 g, 8.2 mmol) was added to a suspension of sodium hydride (0.52 g, 40.9 mmol) and dry DMF (6 ml) at room temperature. The solution was then heated to 110°C for 2 hours with a vigorous stirring. After cooled to room temperature, 1H,1H,2H,2H,3H,3H-perfluorohexane *p*-toluensulphonate (1) was added. The mixture was then heated to 50°C and stirred for 2 hours. The mixture was stirred at 120°C for 15 hours. After cooled to room temperature, water was added. The organic layer was extracted with ether. The extract was washed with distilled water, and the solution is dried over anhydrous Na_2SO_4. The mixture was purified by column chromatography (silica-gel, CH_2Cl_2: Hexane = 6: 5, Rf = 0.8). to yield a white crystal solid (5.86 g, 86%), ^{1}H-NMR ($CDCl_3$, TMS, 500 MHz) δ (ppm) 2.10–2.14 (m, 4H, $-CH_2CH_2C\underline{H_2}C_6F_{13}$ or $-CH_2C\underline{H_2}CH_2C_6F_{13}$), 2.29–2.39 (m, 4H, $-CH_2CH_2C\underline{H_2}C_6F_{13}$ or $-CH_2C\underline{H_2}CH_2C_6F_{13}$), 4.07 (t, $J = 6$ Hz, 4H, $-C\underline{H_2}CH_2CH_2C_6F_{13}$), 6.89–6.91 (m, 2H, Ar$\underline{H}$), 6.92–6.95 (m, 2H, Ar$\underline{H}$), m.p.: 50.5°C 2,3,6,7,10,11-hexakis(1H,1H,2H,2H,3H,3H-perfluorononyloxy)triphenylene (F6/C9) was synthesized by the oxidation of 1,2-fluoroalkoxybenzene with $FeCl_3$ [10,11]. Dry dichloromethane 70 ml was stirred for 1 hour under Ar flow. 1,2-Di(1H,1H,2H,2H,3H,3H-Perfluorononyloxy)benzene (1.03 g, 1.2 mmol) was dissolved in dichloromethane and stirred for 15 minutes in a ice-bath. $FeCl_3$ (0.53 g, 3.3 mmol) and the five drops of H_2SO_4 were added in the mixture and stirred for 23 hours. Methanol (100 ml) was added in the mixture and stirred for 30 minutes. The mixture was evaporated only dichloromethane (0.046 MPa, 30°C) and left over the overnight in a refrigerator. The residue was purified by chromatography (ϕ60, $l = 25$ cm, silica-gel, chloroform: hexane = 3:1, Rf = 0.6) and recrystallized from 1,3-bis(trifluoromethyl)benzene-methanol (1:1) to yield a white crystal solid (0.22 g, 22%). ^{1}H-NMR ($CDCl_3$, TMS, 500 MHz) δ(ppm) 2.22–2.27 (m, 12H, $-CH_2CH_2C\underline{H_2}C_6F_{13}$ or $-CH_2C\underline{H_2}CH_2C_6F_{13}$), 2.39–2.49 (m, 12H, $-CH_2CH_2C\underline{H_2}C_6F_{13}$ or $-CH_2C\underline{H_2}CH_2C_6F_{13}$), 4.32 (t, $J = 6$ Hz, 12H, $-C\underline{H_2}CH_2CH_2C_6F_{13}$), 7.82 (s, 6H, Ar$\underline{H}$), FT-IR (KBr, cm^{-1}) 1619, 1520, 1441, 1265, 1236, 1206, 1189, 1144, 1033, 839, 698, 655.

F6/C9 shows a Col$_{hd}$ mesophase between 90°C and 183°C [9]. The corresponding hydrocarbon homologue, C9OTP has 57°C and 78°C for the melting and clearing points, respectively (Table 1) [12].

The carrier mobility in the Col$_{hd}$ mesophase was evaluated by a TOF technique. The sample cell for the TOF measurement is consisting of two ITO-coated glasses separated by polyimide films as spacers (12.5 µm-thick). The sample was injected into the cell gap at a temperature of the isotropic phase by capillarity action. A homeotoropic alignment was obtained on gradual cooling from the isotropic phase

Table 1. Phase transition behavior of F6/C9 and C9OTP

Compound	Phase transitions				
F6/C9	Cr	90°C (63.2 kJ/mol)	Col$_{hd}$	183°C (6.4 kJ/mol)	Iso
C9OTP	Cr	57°C (71.1 kJ/mol)	Col$_{hd}$	78°C (2.7 kJ/mol)	Iso



(a)

(b)

Figure 2. Photocurrent decay curves for the fast component in Col$_{hd}$ mesophase at 180°C (a) for positive carrier and (b) for the negative carrier.

[13]. Bias voltage was applied across the sample cell and a N_2 pulsed laser was used as the excitation light source ($\lambda = 337\,nm$, pulse width $= 800\,ps$). The mobility was calculated by the following equation $\mu = d^2/t_\tau V$ (μ: mobility, d: Electrode distance, t_τ: transit time, V: applied voltage). The details of TOF measurement are described elsewhere [14].

3. Result and Discussion

Figure 2 (a) shows transient photocurrent decay curves for the positive carriers in which one can observe well-defined transit-times. The carrier mobility was calculated to be $3.7 \times 10^{-4}\,cm^2\,V^{-1}\,s^{-1}$ at 180°C. On the other hands, Figure 2 (b) shows the mobility of the negative carriers, calculated to be $3.6 \times 10^{-4}\,cm^2\,V^{-1}\,s^{-1}$ and these results is almost the same as for the positive carriers, meaning an ambipolar property. This characteristic of F6/C9 is the same as that of the corresponding hydrocarbon homologue [15]. In addition, it was observed for the negative carriers that the

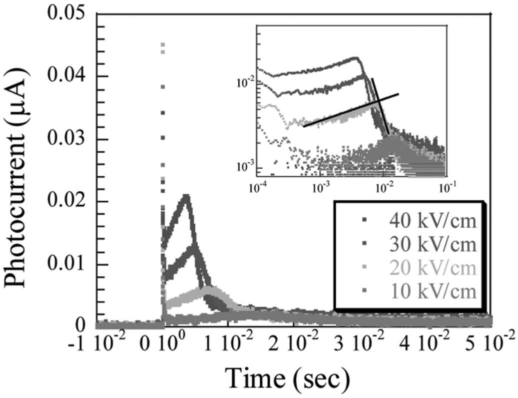


Figure 3. Photocurrent decay curves of negative carrier for the slow component in Col$_{hd}$ mesophase at 180°C.

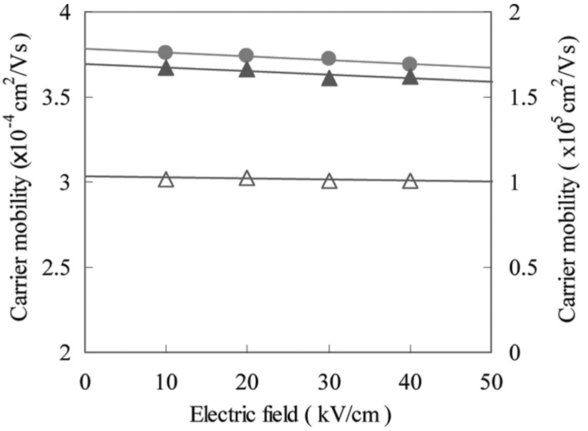


Figure 4. Applied field dependence of the carrier mobility in the $\mathrm{Col_{hd}}$ mesophase at 180°C. Closed circles: positive carrier, closed triangles: negative carrier of the fast component and open triangles: negative carrier of the slow component.

photocurrent decay curves consist of slow and fast components. The carrier mobility for the slow component was calculated to be $1.0 \times 10^{-5}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ as shown in Figure 3. This is probably due to ionic carrier transports derived from O_2 and H_2O contained in the sample.

These carrier mobilities were essentially independent of the applied electronic field as shown in Figure 4 and this is a common characteristic for discotic liquid crystalline semiconductors [16]. Furthermore, these characteristics are almost the same as those of the hydrocarbon homologue (C9OTP).

Consequently, the mobility of F6/C9 in the $\mathrm{Col_{hd}}$ mesophase is not increased in comparison to that of C9OTP. However, the thermal stability of columnar phase is higher than that of C9OTP. The lattice constant of the F6/C9 was calculated to be 27.6 Å (Fig. 5). This value is slightly increased comparing to the C9OTP (24.5 Å), implying the interdigitation of chains is limited in F6/C9 probably due to the fluor-

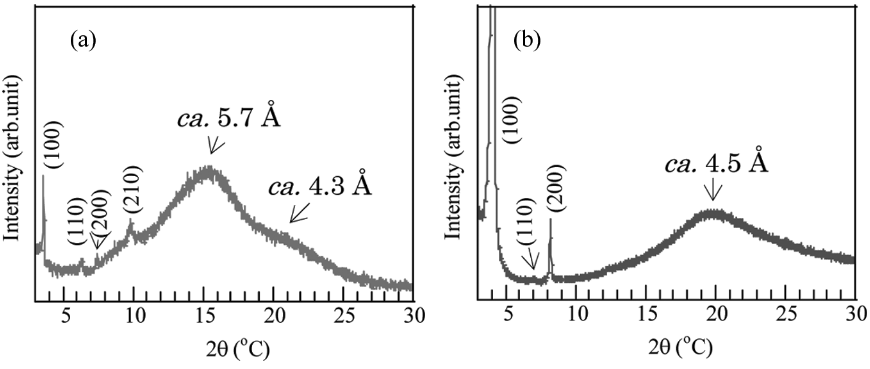


Figure 5. Powder X-Ray diffraction patterns of $\mathrm{Col_{hd}}$ mesophases of the (a) F6/C9 at 170°C and (b) C9OTP in the $\mathrm{Col_{hd}}$ mesophase at 75°C.

ophilic/fluorophobic interactions. Additionally, in the wide-angle region, two diffused reflections come up at *ca.* 4.3 Å and *ca.* 5.7 Å corresponding to the liquid-like order of the hydrocarbon aliphatic chains [17] and of the perfluoroalkyl chains [18–20], respecting and the former is seen the C9OTP indicating the molecular stacking of core parts in column is rather disordered. Considering the result of XRD measurements, the thermal stability of Col_{hd} mesophase was stabilized by fluorophilic/fluorfluorophobic interactions which induce a nano-segregated structure in a column. On the other hand, the mobility behavior in the Col_{hd} mesophases is common in both F6/C9 and C9OTP and this is reasonably suggested by the carrier mobility values is the same order.

4. Conclusion

The carrier mobility in the Col_{hd} mesophase of a perfluoroalkylated triphenylene derivative (F6/C9) was evaluated by TOF measurements. F6/C9 shows an ambipolar character and, the positive and negative carriers are in the order of 10^{-4} cm^2 V^{-1}s^{-1}. Also for the negative carriers, the slow component could be observed in the decay curves corresponding to the mobility in the order of 10^{-5} cm^{2}V^{-1}s^{-1}, probably due to the ionic transport. The carrier mobility is independent of the applied field ranging from 10 kV/cm to 40 kV/cm. These carrier transport properties are almost identical to those of the corresponding hydrocarbon homologues (C9OTP).

XRD measurements indicate that the mesophase formed by F6/C9 is a hexagonal disordered columnar (Col_{hd}) mesophase, and it is almost comparable to that of C9OTP. Though the fluorophilic/fluorophobic interactions among the peripheral chains stabilize the columnar structure, the stacking of triphenylene core along the columnar axis in F6/C9 is a disordered state which is just the same situation on C9OTP. It is reasonable to think that the observed carrier mobility of F6/C9 is in the comparable order to that of C9OTP.

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