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Fast Carrier Mobility in Smectic A Phase of a Liquid Crystalline Compound Containing an Imidazolium Salt

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*A smectogenic 1,3-bis(4-decyloxyphenyl)-3H-imidazol-1-ium trifluoromethane sulfonates (***1***) was studied on the drift mobility of carriers by a Time-Of-Flight (TOF) technique. The transient photocurrent decay curves were clearly observed for the positive electrode illumination and the transit times could be detected to indicate the mobility in the smectic A (SmA) phase is on the order of* 10^{-3} cm^2 V^{-1} s^{-1}*. This carrier mobility is too fast if it is a reflection of ionic transport in this system and is more easily explained on the basis of electronic charge hopping process.*

Keywords Carrier mobility; imidazolium salt; ionic liquid; liquid crystal; organic semiconductor

Introduction

Liquid crystalline semiconductor is now one of the most interesting topics as organic semiconductors as well as liquid crystals because of its high solubility into common organic solvents and to self-assembling nature which are required on the wet processing of film device fabrications [1]. On the other hand, ionic liquid such as imidazolium salts have been extensively studied in terms of a novel type of organic electrolytes [2] and recent studies aiming to give functional properties to ionic-liquid-based compounds have shown that it is good as a liquid crystalline molecule [3].

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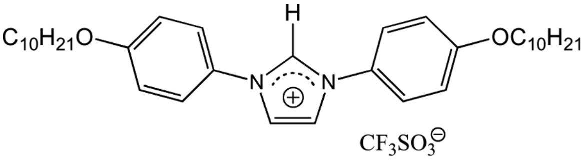
In addition, the diversity of chemical structures of liquid crystalline compounds with the skeleton of imidazolium salts nowadays covers discotic as well as calamitic (rod-like) liquid crystals [4]. For both cases, the chemical structures were sometimes designed to construct both ionic and electronic charged carrier transports in the mesophase to study the potential applications to organic electronics [5].

Recently, a series of liquid crystalline imidazolium salts, 1,3-bis (4-alkoxyphenyl)-3*H*-imidazol-1-ium trifluoromethane sulfonates, were synthesized to show a smectic mesomorphism, where smectic layered structures are stabilized by electrostatic interactions [6]. Furthermore, preliminary results of carrier mobility measurements by a Time-Of-Flight (TOF) technique showed it is in the order of $10^{-4}\,cm^2\,V^{-1}\,s^{-1}$ in the smectic A phase [7].



Cryst 115°C SmA 160°C Iso

1

In this work, the decyloxy homologue **(1)** was studied in terms of an electronic hopping transport of carriers in mesophase by a TOF technique to indicate that the electronic hopping process could be active in the SmA phase of ionic liquid crystals.

Experimental

Synthesis of the compound **1** was carried out by the procedure reported elsewhere [7]. The product was purified by repetitive recrystallizations from solution. The carrier mobility was determined by a TOF technique. N_2 laser shots (337 nm) with 800 psec width of pulse were manually operated to the compound in a sandwich-type cell (with *ca.* 15 µm-thick film as spacer). The cell electrodes were a set of ITO and TiO_2 to inject the carriers into the compound from the charge generation layer of TiO_2 as any optical absorptions were undetectable at 337 nm for **1**. The mobility μ was calculated by the observed transit time, t_τ following the equation below,

$$\mu = d/t_\tau E$$

where d and E are a distance between two electrodes and applied field, respectively. The experimental details were described in Ref. [8].

Results and Discussion

Figure 1 shows the transient photocurrent decay curves obtained for the SmA phase (120°C) with variant applied electric fields in the positive electrode illumination. The negative electrode illumination did not give any response in the photocurrent detection. The double logarithmic plots of decay curves exhibit not so clear decays as an ideal one. However, the transit time of carriers could be determined to give the drift mobility in the order of $10^{-3}\,cm^2\,V^{-1}\,s^{-1}$ for the SmA phase. The applied field

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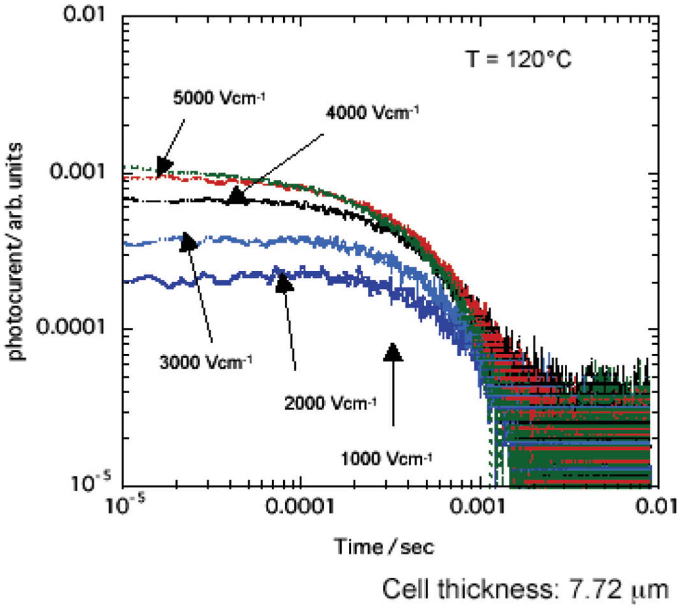

Figure 1. Transient photocurrent decay curves of **1** at 120°C (SmA phase) obtained for the positive electrode illumination in a TOF measurements.

dependence of t_τ is seen as shown in Figure 2. It is found that the positive carrier mobility is field-dependent and this is not of typical as liquid crystalline semiconductors [9].

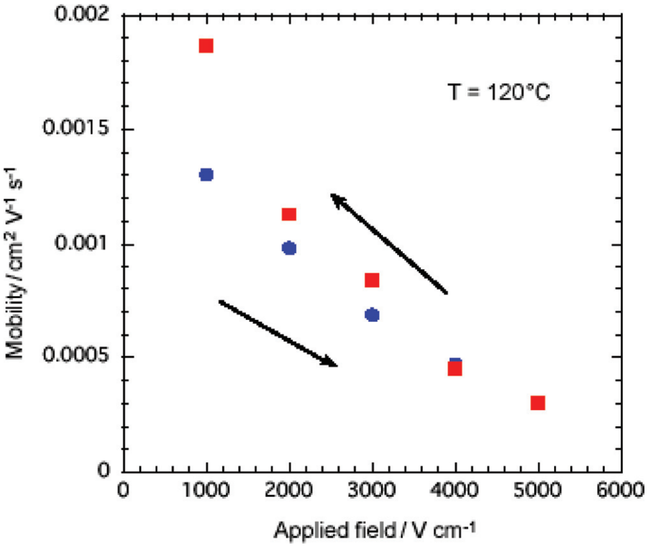

Figure 2. Applied field dependence of the carrier mobility (positive) at 120°C. The measurements started and ended at 1000 V/cm, indicated by arrows.

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The applied field dependence of mobility showed a reversible manner for the change of field sign. The mobility is decreased as the field increases and *vice versa*. This is just the opposite case for amorphous organic semiconductors, where one can see the increased mobility with the increased field. The ionic moieties contained in this molecule is reasonably expected to show the current derived from the ionic transport on the electric field. This leads to a loss of the field applied for electronic hopping in the system. Thus, the effective field should be less than the applied one. This situation that ions transport in a field to the counter electrodes does, more or less, make one consider how the variant field in micro-scaled area due to the mobile ions affect the charged species which contribute to the electronic hopping process.

The time scale of charge hopping phenomenon is in the order of less than *pico* second and on the other hand, ionic transport is a phenomenon in the less order of $10^{-4}\,\mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{s}^{-1}$ even for the less viscous nematic phase [10]. This means that the charged species hopping among molecules could not recognize the slowly transporting ionic carriers as a variant field when they hop from molecule to molecule. The transporting ionic species in the system could behave as shallow and deep traps for hopping charges and furthermore, the local field formed by ionic species can be described as a distribution of local field. It is essentially important to see that the non-dispersive decay of photocurrent was actually observed in the TOF measurements for this compound. As the case of SmA phase, domain boundaries hardly affect the drift mobility of carriers, meaning the boundaries do not behave as deep trap sites for the carriers. Thus, the fact that not so clear transient decay curves were observed are probably due to the impurities in addition to the ordered ionic parts of molecules in the layered structures.

In these measurements, the drifting charges give the transient photocurrent decay within a certain range of time. Also it should be noticed that there was no other transit time in the slower time range probably derived from ionic transport, which is sometimes detected as an additional step in the decay curves resulting in the mobility in the order of $10^{-5} \sim 10^{-6}\,\mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{s}^{-1}$ [11,12]. The number of ionic carries essentially is corresponding to the twice number of molecules in the system and the amount of ionic species is far more than that of the generated and injected charges in the TOF condition. One more situation one could be considered is that the ionic species, especially the triflate anions steadily stay around the counter positive imidazolium ions arranging in a manner of layered structure and this structured ionic species may not be difficult to electrostatically affect the path for charge hopping, as the phenyl groups could be considered to be a main path for charge hopping (Fig. 3).

Furthermore, it should be also noticed that the purification of this compound resulted in the improved mobility by one order of magnitude ($10^{-4}\,\mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{s}^{-1}$ [7] to $10^{-3}\,\mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{s}^{-1}$ in this work). Actually, the mobility in the order of $10^{-3}\,\mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{s}^{-1}$ is surely too fast to interpret this was attained by ionic transport and the observed mobility is rather faster than that ever observed for SmA phase ($\sim 10^{-4}\,\mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{s}^{-1}$).

The influence of ionic impurities involving in liquid crystalline semiconductors was discussed to give results possibly doubtful, but once to provide the information of spatiotemporal evaluation of ionic charge densities under bias [13]. On the other hand, it was reported that the TOF technique could present the information of ion mobility during a curing process of polymers [14,15].

Recent report on SEM image of ionic liquid, an imidazolium salt, interestingly implies the possibility of electronic process is active for such an electrolyte [16] and

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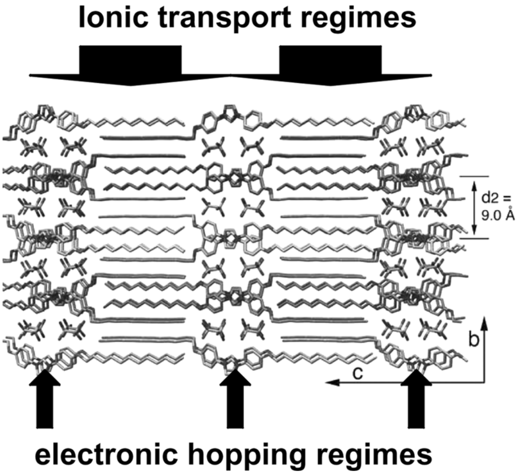

Figure 3. A schematic representation of a common concept for the charged carrier transport of ionic and electronic processes in a smectic-layered mesophase of **1**.

actually the authors describe the charge-up phenomenon could not be seen which is often seen for insulating organic materials and gets worth situation for obtaining the image.

These suggest that in the SmA phase of ionic liquid crystals an electronic hopping process for carrier transport could be active even though involving ionic moieties in a mesogenic molecule and could be enhanced by electrostatic interactions among the ionic moieties.

Conclusion

The transient decay curves for the positive electrode illumination were observed in TOF measurements of carrier mobility for a SmA phase exhibited by a calamitic liquid crystal containing an imidazolium triflate. This is in one sense very strange because ionic impurities forms trap sites in the system and prevent the carrier drifting, leading to the ambiguous decay curves difficult to determine the transit time or the diminished current to be undetectable. Also the order of mobility evaluated to be $10^{-3}\,\mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{s}^{-1}$ is too high for ascribing to ionic transport process. It might be observed that charge hopping among molecules is realized even in such an ionic media formed by ionic liquid crystals and this might be due to the ordering of ionic parts of molecules in such a layered structure. These indicate the possibility of electronic hopping process should be considered in SmA phase of ionic part containing liquid crystalline materials. Further studies are in progress.

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