



Charge carrier transport in liquid crystals



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ABSTRACT

The materials exhibiting charge carrier mobility ranging from 10^{-3} to $0.1 \text{ cm}^2/\text{Vs}$, i.e., between those of amorphous and crystalline materials, had been missing before the 1990s when the electronic conduction in liquid crystals was discovered. Since then, various liquid crystalline materials including discotic and calamitic liquid crystals have been studied in order to clarify their charge carrier transport properties in liquid crystalline mesophases. In this article, the historical background of the discovery of electronic conduction in liquid crystals, intrinsic and extrinsic conduction, unique properties of the charge carrier transport, the effect of molecular alignment on it, and the conduction mechanism in liquid crystalline mesophases are shortly described on the basis of the experimental and theoretical studies accumulated in these two decades, noting that the missing materials were liquid crystals.

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1. Introduction

The charge carrier transport in liquid crystals had been thought to be ionic for a long time before the electronic conduction was established in both discotic (disk-like) and calamitic (rod-like) liquid crystals in the 1990s [1–3]. Indeed there is a historical reason to believe it: in the late 1960s, Heilmeyer in RCA proposed a display device with a liquid crystal based on the so-called dynamic scattering mode [4], which is quite different from the display devices used in PC monitors and TV sets today and gives an optical contrast derived from light scattering by dynamic motion of aligned liquid crystalline molecules agitated by ions drift under a given applied bias; because of this attractive display device at that time, a lot of measurements were carried out in order to characterize electrical properties of liquid crystals [5–7]. As a result, it led to a general recognition that the electrical properties in liquid crystals were governed by ionic conduction. In fact, the establishment of electronic conduction in liquid crystals was achieved not in calamitic liquid crystals [8] but in a discotic liquid crystal after its discovery in 1977 [1]. The reason why we often observe the ionic conduction in liquid crystals is that the intrinsic conduction in liquid crystals is easily degraded into the ionic conduction by trace amounts of chemical impurities as is described later on.

As for the organic semiconductors in the early 1990s, that is, before the discovery of electronic conduction in liquid crystals, the organic semiconductor materials were categorized into two types of molecular aggregates, i.e., amorphous solids and crystals. Their mobilities are in the range below $10^{-4} \text{ cm}^2/\text{Vs}$ and over $10^{-1} \text{ cm}^2/\text{Vs}$, respectively as shown in Fig. 1. The materials exhibiting the mobility in the range from $10^{-4} \text{ cm}^2/\text{Vs}$ up to $10^{-1} \text{ cm}^2/\text{Vs}$ were missing at that time.

In this article, the unique carrier transport properties in liquid crystals highlighted on calamitic liquid crystals are described in comparison with those of organic amorphous and crystalline materials, and it is shown that they are well explained by the molecular alignment not so ordered as those in crystals and not so disordered as those of amorphous solids. Then, the final conclusion of this article naturally indicates that the missing materials in Fig. 1 are the liquid crystals.

2. Electronic and ionic conduction in liquid crystals

As described above, the intrinsic charge carrier transport properties in liquid crystals is governed by electronic conduction, in which electrons and holes are charge carriers. However, it is quite sensitive to chemical impurities responsible for charge trap states and easily degraded into ionic conduction, in which ionized molecules and atoms are transported as carriers. In addition, in order to understand why the ionic conduction in liquid crystals is so often observed, it is very important to notice that the ions in liquid crystals are not always the ions dissociated from ionic impurities but neutral chemical impurities, e.g., by-products of synthetic reactions, both of which often contaminate liquid crystals during their synthesis. In fact, it is relatively easy to remove the ionic impurities rather than the neutral ones by recrystallization and distillation.

The transient photocurrents shown in Fig. 2 demonstrate how the chemical impurities affect the conduction in liquid crystals, in which a 2-phenylnaphthalene derivative of 2-dodecyloxy-6-(4-octylphenyl)naphthalene (8-PNP-O12) highly purified and a terthiophene derivative of ω,ω' -dihexyl terthiophene (6-TTP-6) are used as a host liquid crystal and an impurity molecule for electrons and holes, respectively [9]. As long as the host liquid crystal is not contaminated with the terthiophene derivative, a non-dispersive and well-defined transient photo current is observed and exhibits a transit time as a shoulder as

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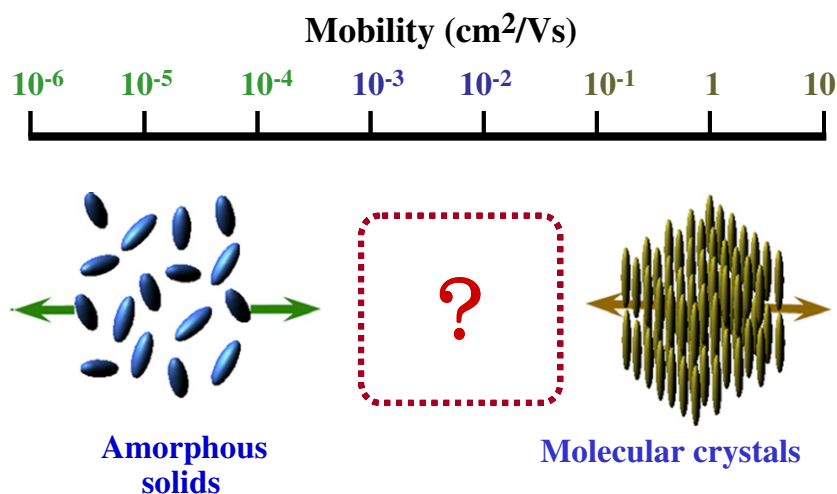


Fig. 1. Organic semiconductor materials and their mobility in early 1990s. The materials exhibiting the mobility in the range of 10^{-4} cm^2/Vs to 10^{-1} cm^2/Vs were missing.

shown in Fig. 2. However, once the liquid crystal is contaminated with a trace amount of the terthiophene derivative of 1 ppm, the transient photocurrent becomes dispersive and gives an additional shoulder at a slow time range, as indicated by the 2nd transit in the figure. Furthermore, the transient photocurrent in a 50 ppm doped sample gives only one shoulder at the same slow time range as in the 1 ppm doped sample [9,10]. Judging from the temperature and field dependence of the mobility, in addition to the dilution experiment with a hydrocarbon described later on, it is concluded that the slow transit is due to the ionic conduction originating from the terthiophene molecules either by photo-ionization and/or auto-ionization or by trapping charges. This result clearly indicates how easy the electronic conduction is degraded into the ionic conduction.

The ionic conduction depends on the viscosity of the media where ions are transported, so that highly ordered smectic liquid crystalline phases are relatively less sensitive to impurities in terms of the ionic conduction, while the less ordered ones such as the nematic phase, smectic A, and C phases favor for the ionic conduction [9–11]. In fact, the electronic conduction can be often observed even in the contaminated samples in highly ordered smectic phases, although the mobility becomes smaller and trap-controlled by the impurities. This is true also in polymeric liquid crystals because of their high viscosity [12].

As far as the electronic and ionic conduction are concerned in liquid crystalline mesophases, it is not always easy to distinguish the electronic condition from the ionic one in a particular system by a value of

the mobility itself: the mobility on the order of 10^{-3} cm^2/Vs or higher at ambient temperatures is surely attributed to electronic conduction; on the other hand, it is not easy to judge the conduction regime, i.e., electronic or ionic conduction, from the mobility, when the mobility is less than 10^{-4} cm^2/Vs ; in fact, the typical mobility for the ionic conduction in the liquid crystals is 10^{-5} cm^2/Vs to 10^{-6} cm^2/Vs , which is also a typical mobility observed in the liquid crystals having a large dipole moment. Therefore, we need additional experiments to judge what conduction governs in a particular liquid crystal.

One of the convenient methods to judge the conduction regime is the dilution experiments with a hydrocarbon of low molecular weight that exhibit far lower viscosity than those of liquid crystals: when the electronic conduction is responsible for charge transport from molecule to molecule, the mobility in a diluted system is decreased because of an average molecular distance increased by dilution; on the other hand, the mobility is increased when the ionic conduction governs the charge transport, because the ionic mobility in the diluted system is increased due to a lower viscosity after dilution, which is expected in Eq. (1) for Walden's rule [13], where μ is the mobility, η is a viscosity of the media, r is the ion radius, and m is a constant.

$$\mu\eta^m = \frac{e}{6\pi r} \quad (1)$$

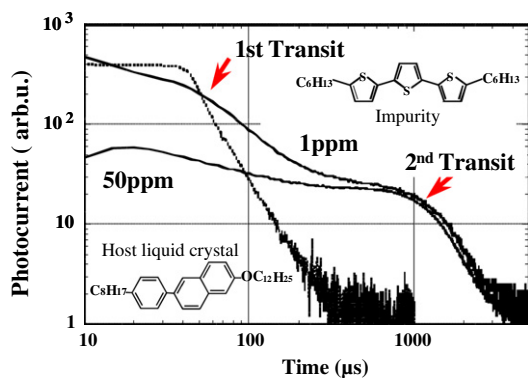


Fig. 2. Transient photocurrents for hole in SmA phase of 2-phenylnaphthalene derivative of 8-PNP-O12 doped with a terthiophene derivative of 6-TTP-6. Transient photocurrents were measured at 110 °C for SmA phase by time-of-flight experiments with liquid crystal cells capillary-filled with a given mixture of 8-PNP-O12 and 6-TTP-6.

A typical example for the dilution experiments is shown for negative charge transport in a liquid crystalline 2-phenylnaphthalene derivative of 8-PNP-O12 in Fig. 3 [14]. In both SmA and SmB phases, the fast and slow transits of carriers are observed: it is very clear that the fast transits do not depend on temperature, while the slow transits do; in the system with dodecane, it is very clear that the fast mobility is decreased slightly irrespective of smectic phase, but the slow mobility is increased significantly, accompanied with a clear reduction of activation energy; on the other hand, the mobility in the isotropic phase is kept almost unchanged. Therefore, the fast mobility in each smectic phase is attributed to the electronic conduction and the slow one is to that of the ionic conduction. It should be noted that the change in mobility is obvious in the ionic mobility rather than the electronic one. This is due to the segregation of dodecane into the interlayers of the microphase-separated structure in the smectic mesophase, in which flexible hydrocarbon chains of liquid crystalline molecules are aggregated and ions are transported. This segregation effectively reduces local viscosity and favors the ionic conduction. All these facts indicate that the conduction channels for electrons and holes and for ions are spatially localized, or separated, in other words, there are two intrinsic conduction channels in smectic

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