

High Carrier Mobility up to $0.1 \text{ cm}^2/\text{Vs}$ and a Wide Mesomorphic Temperature Range of Alkynyl-Substituted Terthiophene and Quaterthiophene Derivatives

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Smectic semiconductors with high carrier mobility were designed and synthesized. The hole mobility of 3-TTP-yne-4 and 3-QTP-yne-3 at room temperature was $0.06 \text{ cm}^2/\text{Vs}$ and $0.1 \text{ cm}^2/\text{Vs}$, respectively. They exhibit highly ordered smectic phases around room temperature, with softness to some extent, which make it possible homogeneous film with low defect density. Intermolecular distance in the smectic phase of 3-QTP-yne-4 is almost same as that of 3-TTP-yne-4. In this material, larger π -conjugate system results in higher carrier mobility.

Keywords: carrier mobility; disorder model; oligothiophene; semiconductor; smectic phase; time-of-flight technique

INTRODUCTION

Recently development of organic semiconductors is giving rise to organic electronics aiming at flexible display [1]. In organic single crystals with extremely high purity, carrier mobility is usually on the order of $10^{-1} \text{ cm}^2/\text{Vs}$ at room temperature [2]. However, in contrast to the organic single crystals, practical amorphous organic semiconductors which can be applied to thin films with large area, exhibit very low carrier mobility on the order of $10^{-7} \sim 10^{-4} \text{ cm}^2/\text{Vs}$ [3]. This is attributed to energetic and spatial disorder of organic molecules, and

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carrier mobility and its field- and temperature-dependence is described by Gaussian disorder model [4].

In liquid crystal phases, the energetic and spatial disorder, should be reduced by molecular alignment. We have verified fast electronic conduction in smectic liquid crystals with aromatic π -conjugated systems [5–8,10], which has been believed to be ionic for a long time [11], while fast hole transport was observed in discotic columnar phases [12–14]. And we have also demonstrated their applications to opt-electronics devices such as photosensors [15], xerography [16], and light-emitting diode [17].

For practical application, it is indispensable to establish material design to realize high carrier mobility as well as wide mesomorphic temperature range around room temperature. However, lowering mesomorphic temperature range is usually incompatible with fast carrier transport. Fast intrinsic carrier transport is observed only in highly ordered smectic phases, which usually have a tendency to crystallize above room temperature, due to strong π - π interaction. Introduction of lateral substituents is often effective on lowering temperature range of mesophases, however closer molecular packing is usually inhibited, resulting in disappearance of highly ordered smectic phases or low carrier mobility, caused by decrease in transfer integral.

We have already reported that cyclohexylethylterthiophene derivative mixture exhibit smectic phases and fairly good carrier transport in wide temperature range from -100°C to 100°C because of the presence of bulky cyclohexylethyl group inhibiting crystallization [10]. However the smectic phases at room temperature was smectic B hexatic, and the hole and electron mobility was at best on the order of $10^{-3} \text{ cm}^2/\text{Vs}$ at room temperature [10].

In this report, we report oligothiophene derivatives which exhibit highly ordered smectic phases in wide temperature range around room temperature. And we show alkynyl-substituted terthiophene and quaterthiophene derivatives exhibit excellently high carrier mobility up to $0.1 \text{ cm}^2/\text{Vs}$.

MATERIAL DESIGN AND SYNTHESIS

We designed new liquid crystalline semiconductors based on terthiophene and quaterthiophene which are structural units of promising organic semiconductors, oligothiophene derivatives. In general, strong intermolecular π - π interaction increase isotropic-mesophase transition temperature, while increasing crystallization temperature. In fact, dialkylterthiophene [8] and dialkylquaterthiophene [18] crystallize above room temperature. In order to decrease crystallization

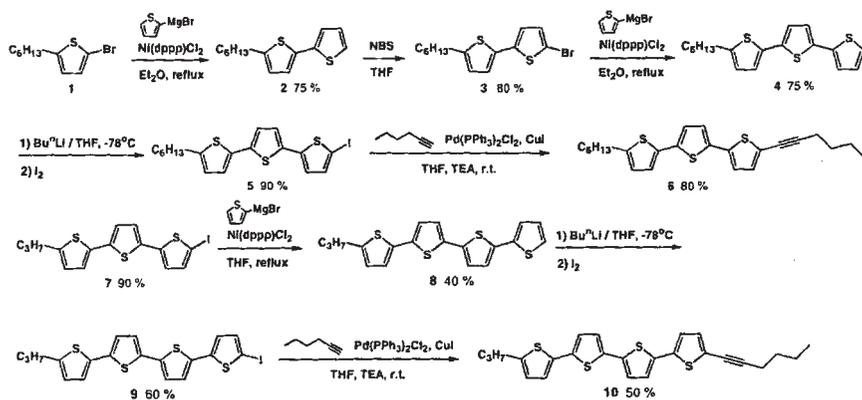


FIGURE 1 Synthetic route of alkynyl-substituted terthiophene and quaterthiophene derivatives.

temperature, introduction of moiety, which cause asymmetry in molecular shape should be effective. Instead of alkyl group, alkynyl group was introduced on 2 position of terthiophene or quarterthiophene skeleton.

As shown in Figure 1, 2-alkyl-5':5':2':2''-terthiophene was synthesized by repeated Tamao coupling reaction catalyzed by Ni(dppp)Cl₂ [19] between thienyl magnesium reagent and thienyl bromide in diethyl ether from 2-alkyl-5-bromothiophene in 3 steps. The obtained alkylterthiophene derivatives was iodinated with iodine after lithiation of the 5'' position of the terthiophene derivatives in THF at -78°C . The iodide was coupled with excessive 1-hexyne were coupled in the presence of triethylamine and catalytic amount of Pd(PPh₃)₂Cl₂ in THF at room temperature, producing 2-alkyl-5''-hexynyl-3:5'-2':2''-terthiophene in the yield of 76%. The iodide was coupled with 2-thienyl magnesium bromide in the presence of catalytic amount of Ni(dppp)Cl₂ in THF under refluxing condition. The obtained 2-alkylquaterthiophene was iodized in the same way. The resulting iodide and excessive 1-hexyne were coupled in the presence of triethylamine and catalytic amount of Pd(PPh₃)₂Cl₂ in THF at room temperature, producing 2-alkyl-5''-hexynyl-2:5'-2':5''-2''-quaterthiophene in the yield of 70%.

Phase Transition Behaviors and Structural Characterization

The phases of the materials were identified by the observation of optical textures under polarized light microscope, miscibility test

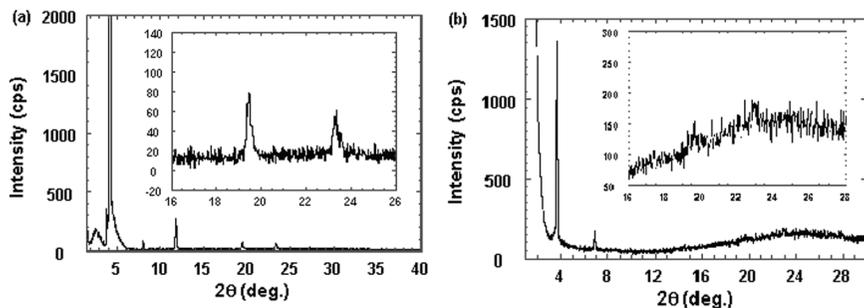


FIGURE 2 X-ray diffraction patterns of (a) 3-TTP-yne-4 and (b) 3-QTP-yne-4 at 30°C.

and X-ray diffraction. Phase transition temperature was determined by differential scanning calorimetry.

These materials precipitate as crystals at room temperature, however highly ordered smectic phases, which are characterized by mosaic optical textures under observation of polarized light microscope, when they are cooled down from isotropic melting liquids. In DSC measurement, only one exothermal peak was observed at 98°C for 3-TTP-yne-4 and at 196°C for 3-QTP-yne-4 cooling from isotropic liquids to -50°C , indicating no signs of crystallization, therefore these three compounds exhibit single smectic phases respectively around room temperature in cooling process.

As shown in Figure 2, diffraction peaks in low angle region associated with layer structures and two weak peaks in high angle region related to molecular order in the smectic layers appear in X-ray diffraction curves of these three compounds. Molecular order within the smectic layers of these three compounds at room temperature is hexagonal, since the ratio of lattice constants in high angle region is approximately $\sqrt{3}/2$. In the cases of 6-TTP-yne-4 and 3-TTP-yne-4, lattice constants of [100] are identical with molecular lengths with all-trans conformation of alkyl chains. Therefore the smectic phase of 6-TTP-yne-4 and 3-TTP-yne-4 can be identified to be smectic B crystal phase. In the case of 3-QTP-yne-4, the constant is shorter than molecular length, and therefore the phase should be characterized to be tilted hexagonal smectic phase, such as smectic G or smectic J phase. The diffraction angles, Miller indices, and lattice constants are listed in Table I.

TOF MEASUREMENT SET UP

Carrier mobility was determined by conventional time-of-flight (TOF) technique, consisting of N_2 pulse laser ($\lambda = 337 \text{ nm}$, pulse

TABLE I X-ray Diffraction Measurement of 3-TTP-yne-4 and 3-QTP-yne-4

3-QTP-yne-4				3-TTP-yne-4			
2θ	θ	[h k l]	d(A)	2θ	θ	[h k l]	d(A)
3.67	1.83	001	24.11	4.20	2.10	001	21.04
6.90	3.45	002	12.80	8.00	4.00	002	11.05
19.70	9.85	100	4.50	19.46	9.73	100	4.56
22.97	11.48	110	3.87	23.30	11.65	110	3.82

duration = 600 ps), digital oscilloscope, and hot stage whose temperature is controlled by PID thermocontroller and on which liquid crystal cell made from two ITO coated glass plates, is fixed. In this method, transit time, t_T is determined from a kink point in transient photocurrent induced by drift of photo-generated carriers. Carrier mobility, μ is determined as drift velocity of carriers per unit electric field, and therefore μ is calculated as Eq. (1).

$$\mu = \frac{d^2}{Vt_T} \quad (1)$$

where d is sample thickness and V is applied voltage.

The liquid crystal molecules aligned parallel to the electrode surfaces, and no change in molecular alignment was observed under polarized light microscope when electric field was applied to the cells. Therefore carrier transport within smectic layers should be observed under the condition.

CARRIER TRANSPORT CHARACTERISTICS OF 3-TTP-YNE-4

First, carrier transport characteristics in the $\text{SmB}_{\text{cryst}}$ phase of 3-TTP-yne-4 is studied with TOF technique from 90°C to -100°C . The hole mobility which was clearly determined in the whole temperature range, and its field- and temperature-dependence is discussed.

Figure 3 shows transient photocurrent curves for hole at 30°C . Non-dispersive transient photocurrent is observed. From these curves, field-independent mobility is obtained to be $6 \times 10^{-2} \text{ cm}^2/\text{Vs}$, which was larger than those observed in the highly ordered SmE and SmG phases of 2-phenylnaphthalene and dialkylterthiophene derivatives and the hole mobility in the discotic columnar plastic phase of hexaalkoxytriphenylene derivatives [12,13].

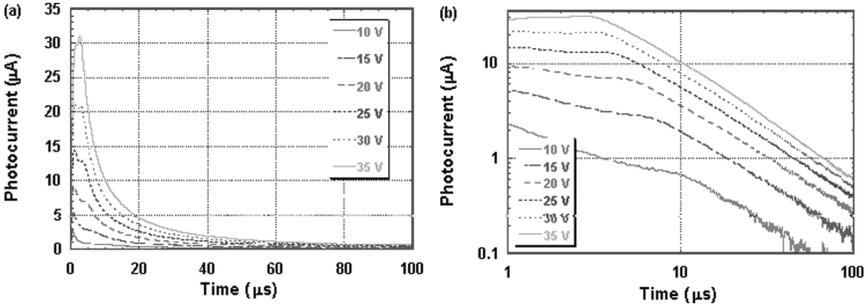


FIGURE 3 Transient photocurrent curves for hole in the $\text{SmB}_{\text{cryst}}$ phase of 3-TTP-yne-4 at 15°C . The cell thickness was $25\ \mu\text{m}$, excitation wavelength $337\ \text{nm}$. (a) linear plot (b) double logarithmic plot.

And the hole mobility is independent of electric field and temperature above -20°C , which is similar to those of the smectic phases of these materials above room temperature. This result indicates that fast electronic conduction is dominant in the $\text{SmB}_{\text{cryst}}$ phase of this compound.

However, the carrier mobility decreases with decrease in temperature, being field- and temperature-dependent below -20°C . As shown in Figure 4, non-dispersive transient photocurrent curves are still observed, suggesting intrinsic carrier transport even below room temperature, however carrier transport mechanism might become different from those above -20°C . In addition, the temperature- and electric-field-dependence of the hole mobility becomes more remarkable with decrease in temperature.

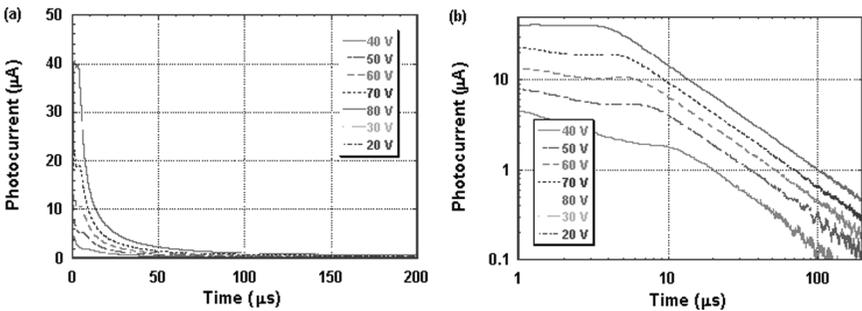


FIGURE 4 Transient photocurrent curves in $\text{SmB}_{\text{cryst}}$ phase of 3-TTP-yne-4 at -50°C . The cell thickness was $25\ \mu\text{m}$, excitation wavelength $337\ \text{nm}$. (a) linear plot (b) double logarithmic plot.

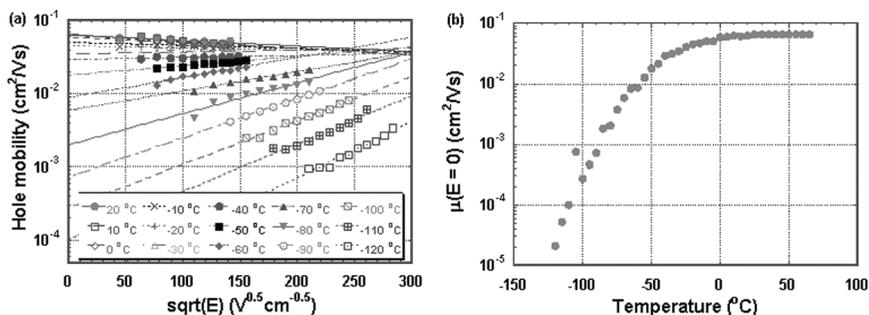


FIGURE 5 Carrier mobility as a function of (a) electric field and (b) temperature.

Figure 5 exhibits temperature- and electric-field-dependence of carrier mobilities. Above -20°C , carrier mobility is independent of electric field and temperature. However the dependence is remarkable below room temperature, and field-dependence becomes larger with decreasing temperature. This behavior is quite similar to those of hopping conduction in amorphous organic semiconductors, which can be described by Gaussian disorder model [4]. Therefore the field-dependence of hole mobility below -20°C is analyzed based on Gaussian disorder model.

ANALYSIS OF CARRIER TRANSPORT CHARACTERISTICS BASED ON DISORDER MODEL

In Gaussian disorder model [4], assuming gaussian distribution of energy levels of hopping sites, and thermal activation of carriers relaxed in the distribution to transport level, based on carrier hopping between molecules, carrier mobility μ is expressed as shown in Eq. (2),

$$\begin{aligned} \mu &= \mu_0 \cdot \exp\left[-(a\hat{\sigma})^2\right] \cdot \exp\left[C(\hat{\sigma}^2 - \Sigma^2)\sqrt{F}\right] \quad \Sigma \geq 1.5 \\ \mu &= \mu_0 \cdot \exp\left[-(a\hat{\sigma})^2\right] \cdot \exp\left[C(\hat{\sigma}^2 - 2.25)\sqrt{F}\right] \quad \Sigma \leq 1.5 \end{aligned} \quad (2)$$

where F electric field, T temperature, and C is constant. Preexponential factor μ_0 corresponds to transfer integral. Disorder parameter σ is width of the gaussian distribution of orbital levels. Σ is associated with spatial disorder. In three dimensional transport as observed in amorphous organic solids, coefficient a is $2/3$, however a should be 0.8 in this two dimensional transport restricted within smectic layers [20] which has been confirmed by trapping effect.

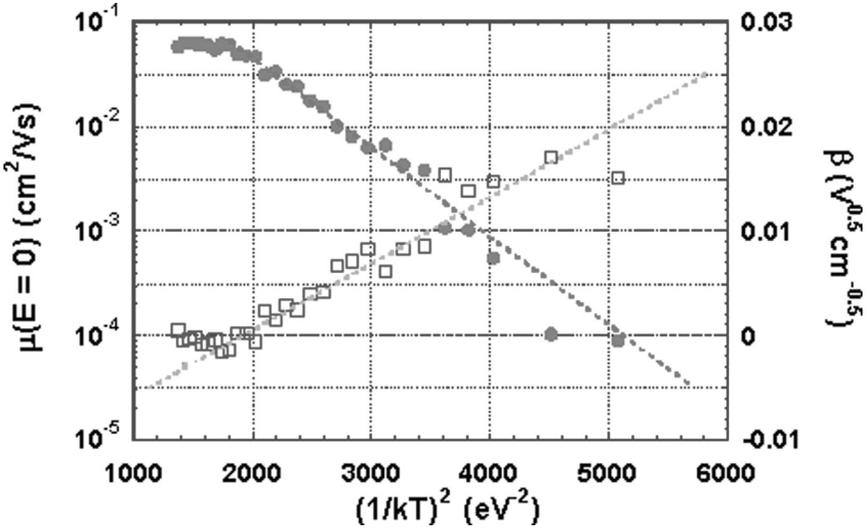


FIGURE 6 μ_0 and β as a function of $1/kT^2$.

In contrast to carrier mobility independent of electric field and temperature above -20°C , logarithm of hole mobility is proportional to square root of electric field, and their dependence increases with decrease of temperature below -20°C .

Figure 6 exhibits μ at zero field and the coefficient $\beta = \partial\mu/\partial F = C(\sigma^2 - \Sigma^2)$, the dependence of carrier mobility on electric field as a function of temperature. In the phase, good fits are obtained in these two plots, although data are slightly scattered at low temperature. β increases with decrease of temperature, which is typical behavior of disordered organic semiconductors. From this plot, μ_0 , σ , Σ , and C were determined to be $6.5 \text{ cm}^2/\text{Vs}$, 47 meV , 1.9 , and $2.85 \times 10^{-3} \text{ V}^{0.5} \text{ cm}^{-0.5}$, respectively.

In the smectic phase, disorder parameter σ and Σ are much smaller than those in organic amorphous solids, in which σ is usually 100 meV and Σ is 2.5 . This should be attributed to molecular alignment in these smectic phases, which should cause field- and temperature-independent carrier mobility above room temperature. Carrier mobility without disorder, μ_0 , is on the order of $10^{-0} \text{ cm}^2/\text{Vs}$, which is much larger than amorphous organic semiconductors including molecularly doped polymers and vacuum evaporated triphenylamine derivatives [21]. This large μ_0 should be due to close packing structure and resulting large intermolecular orbital overlap in the highly ordered smectic phase.

The transition from the temperature region where the mobility is field- and temperature-dependent to that where it is independent of field and temperature is observed as the case of cyclohexylethyl-terthiophene mixture. One possibility is that most of photo-generated carriers are thermally excited to transport level in gaussian density of states in high temperature region, resulting in field- and temperature-independent hole mobility. However, the transition temperatures are different between these two systems in spite of almost same σ 's, distribution of the density of states. Freezing of molecular movement may be associated with the transition.

The comparison between this result and that of cyclohexylethyl-terthiophene mixture, which exhibits less highly ordered smectic B hexatic phase, should be noted. In spite of the difference in molecular packing and order between two systems, disorder parameters, σ and Σ are almost same, however μ_0 of the alkynyl-substituted terthiophene, 3-TTP-yne-4 is quite larger than that of the cyclohexylethyl-terthiophene mixture. This fact indicates that increase of transfer integral by closer molecular packing in highly ordered smectic phases should be more effective on increase of carrier mobility, in contrast to the case of the mixture in which bulky substituent inhibits close intermolecular packing.

HIGH HOLE MOBILITY OF 3-QTP-YNE-4 UP TO $0.1 \text{ CM}^2/\text{VS}$

According to the result of 3-TTP-yne-4, the disorders of the highly ordered smectic phase dose not decrease so remarkable. Increase of μ_0 is effective on increase of carrier mobility rather than decrease of disorders. Extension of π -molecular orbital should increase transfer integral, resulting in increase of μ_0 , and thus carrier transport of 3-QTP-yne-4 is investigated.

Figure 7 shows transient photocurrent curves for hole in the smectic phase of 3-QTP-yne-4 with larger π -conjugate system at room temperature. In the case of this compound, slightly dispersive curves with clear kink point are obtained, indicating fast carrier movement with small distribution. The hole mobility at room temperature reaches $0.1 \text{ cm}^2/\text{Vs}$ which is comparable to that of molecular crystals of aromatic compounds [2] and helical phase of hexahexylthiotriphenylene [14], and the highest value among smectic and other discotic semiconductors.

Above room temperature, hole mobility is independent of electric field and temperature also in this compound. This feature is similar to those in the smectic phases of other calamitic semiconductors. This

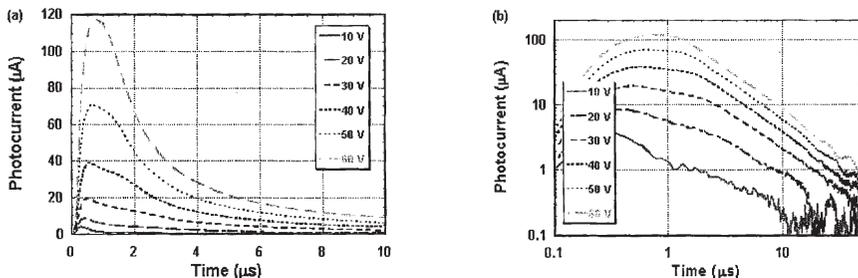


FIGURE 7 Transient photocurrent curves in the highly ordered smectic phase of 3-QTP-yne-4 at 30°C. The cell thickness was 25 μm, excitation wavelength 337 nm. (a) linear plot (b) double logarithmic plot.

result should also be attributed to small energetical and structural disorder in the highly ordered smectic phase.

These compounds exhibit quite high hole mobility at room temperature. In general, carrier mobility both in hopping process and band conduction is determined by transfer integral between molecules, which increases with decrease in intermolecular distance and increase in size of molecular orbitals. The intermolecular distances within smectic layers of these compounds are 3.9 Å, which is smaller than those in smectic phases of other smectic liquid crystalline semiconductors such as 2-phenylnaphthalene [7] and dialkylterthiophene derivatives [8]. Therefore this result should be attributed to close molecular packing structure in the smectic phases, in other words, small intermolecular distance within the smectic layers.

In comparison with discotic columnar phases, it should be remarkable that intermolecular distance within the smectic layers is not so shorter than those of discotic columnar phases. The distance in the smectic phases of 6-TTP-yne-4 and 3-QTP-yne-4 is 3.9 Å, however the typical value of intermolecular distance within columns is 3.6 and 3.5 Å in columnar ordered phase and plastic phase of hexaalkoxytriphenylene derivatives respectively [13]. The distance is merely 3.5 Å even in the helical phase of hexahexylthiotriphenylene which exhibits the highest hole drift mobility of 0.1 cm²/Vs determined by TOF technique [14,21]. In these highly ordered smectic phases, intermolecular charge transfer proceeds more efficiently than discotic columnar phases. The reason is not clear now, however sulfur atom with large van der Waals radius may increase transfer integral, or the two dimensional nature of the carrier transport in these smectic phases may causes different behaviors from one dimensional columnar phases.

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