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# A novel calamitic mesophase semiconductor with the fastest mobility of charged carriers: 1,4-di(5′-octyl-2′-thienyl)benzene†

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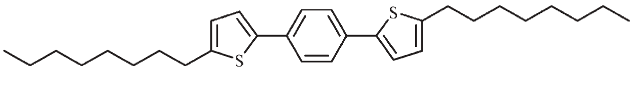
**The carrier mobility of highly ordered lamellar mesophases was evaluated by a Time-of-Flight (TOF) method for mesogenic 1,4-di(5′-octyl-2′-thienyl)benzene (8-TPT-8) to reveal the fastest drift mobility (0.1 cm$^2$ V$^{-1}$ s$^{-1}$ for the lowest temperature mesophase) in calamitic liquid crystals reported to date.**

A new class of organic semiconductors has attracted much attention in recent years.[1] Recent studies of organic semiconductors have shown that the sulfur atom plays a significant role in a close molecular packing and charge carrier transport phenomenon and thus, several attempts have been done to enhance the intermolecular overlap of the molecular orbitals by the introduction of sulfur atoms, in order to obtain a better hopping conduction of charged carriers by the introduction of sulfur atoms. For example, oligothiophenes[2] and regioregular poly(3-hexylthiophene) (P3HT)[3] are known to show comparable high field-effect mobilities of linearly fused polycyclic aromatic compounds such as pentacene and its derivatives.

On the other hand, liquid crystalline semiconductors represent an interesting category of organic semiconductors because of their spontaneous alignment behaviour and good solubility into organic solvents. Adam *et al.*, reported electronic transport of a fast hole mobility of 0.1 cm$^2$ V$^{-1}$ s$^{-1}$ in a highly ordered helical columnar (H) phase of 2,3,6,7,10,11-hexahexylthiotriphenylene that contains six sulfur atoms,[4] which is almost comparable to that of a Si semiconductor. In the case of calamitic liquid crystals as well, Hanna *et al.* reported the case of dialkylterthiophene which self-organizes into a highly ordered Smectic G phase exhibiting a high ambipolar carrier transport in the order of 2 × 10$^{-2}$ cm$^2$ V$^{-1}$ s$^{-1}$ [5] and very recently reported is an asymmetrically substituted quaterthiophene (3-QTP-yne-4) including an acetylene group which exhibits a high mobility up to 1 × 10$^{-1}$ cm$^2$ V$^{-1}$ s$^{-1}$ in a highly ordered smectic mesophase.[6] Additionally, [1]benzothieno[3,2-*b*][1]benzo-thiophene-2,7-dicarboxylate was shown to exhibit a bipolar charge transport with electron and hole mobilities in the order of 2 × 10$^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$ in a kind of smectic A (SmA) phase, a lamello-columnar mesophase where the molecules orient in a smectic layered structure accompanied with a short-range columnar order and this mobility is faster than that of the conventional SmA phase by one order of the magnitude.[7]

However, only one compound showing the carrier mobility faster than 10$^{-1}$ cm$^2$ V$^{-1}$ s$^{-1}$ is found in calamitic mesogens and any certain concept for a molecular design to enhance the carrier mobility has not been attained, in contrast to the theoretical approaches that have been carried out so far for discotic liquid crystals.[8]



8-TPT-8

This work reports a new mesogen, 1,4-di(5′-octyl-2′-thienyl)-benzene (8-TPT-8) exhibiting the fastest mobility of charged carriers in a calamitic mesophase, which contains two sulfur atoms in the molecules, but only two thiophene groups are involved.

8-TPT-8 was obtained in 60% yield by the Stille coupling reaction[9] of 1,4-diiodobenzene and 2-octyl-5-tri-*n*-butylstannyl-thiophene in DMF using 1 mol% of Pd(PPh$_3$)$_4$ as catalyst. The product was purified by column flash chromatography followed by careful recrystallisation several times just before use. We also determined the tin content (<0.1 ppm) by inductively coupled plasma mass spectrometry (ICP-MS).[10]

The liquid crystalline properties of 8-TPT-8 were investigated with polarising optical microscopy (POM), differential scanning calorimetry (DSC) and X-ray diffraction (XRD) analyses. A DSC trace is shown in Fig. 1. It was found that 8-TPT-8 shows three well-ordered mesophases (tentatively called M1, M2 and M3 phases) and the phase transition parameters are shown below. The enthalpies of two phase transitions (from M1 to M2, and from M3 to Crystal phase) are very small and the DSC peaks are so broad like 2nd order phase transition.

The transient photocurrent decay curves obtained with the TOF method showed reasonable shapes of decay (Fig. 2) to evaluate the

| Phase | Cryst | | M3 | | M2 | | M1 | | Iso |
|---|---|---|---|---|---|---|---|---|---|
| Temperature/°C | | 47 | | 71 | | 87 | | 145 | |
| $H$/kJ mol$^{-1}$ | | 2.4 | | 4.8 | | 1.5 | | 32 | |

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† Electronic supplementary information (ESI) available: Hole mobility of 8-TPT-8 as a function of electric field and the XRD table of 8-TPT-8. See http://dx.doi.org/10.1039/b509512n

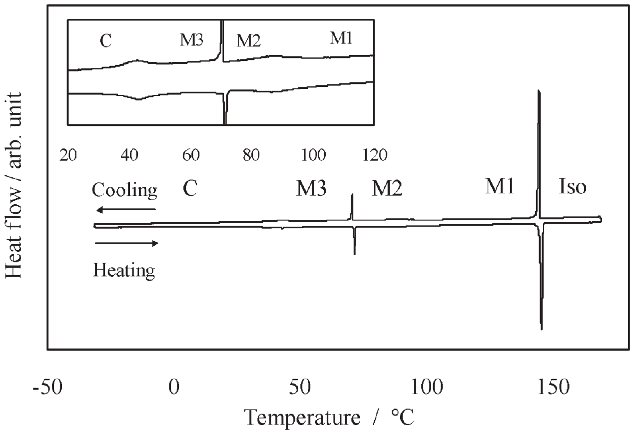

**Fig. 1** DSC traces of 8-TPT-8 (heating and cooling rate: 1 °C $\mathrm{min}^{-1}$) showing enantiotropic phase transitions.

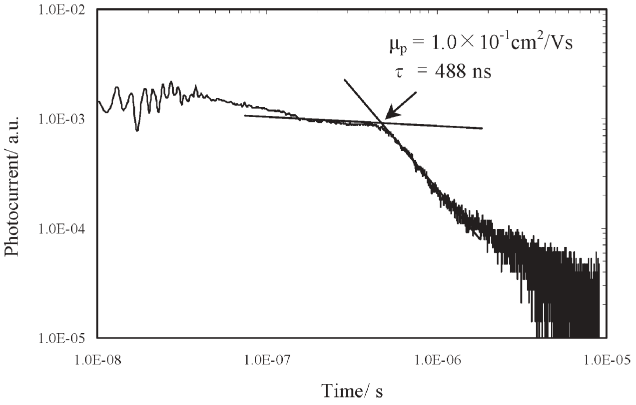

**Fig. 2** A transient photocurrent of the positive charge carriers in the highly ordered mesophase, M3 phase (60 °C) for a ITO/8-TPT-8/ITO cell obtained with the TOF method. The electric field strength was $3 \times 10^4$ V $\mathrm{cm}^{-1}$ (sample thickness: 15.9 μm.)

mobility to be in the order of $10^{-1}$–$10^{-2}$ $\mathrm{cm}^2\ \mathrm{V}^{-1}\ \mathrm{s}^{-1}$ for the three mesophases, as shown in Fig. 3. Especially, the hole mobility at 60 °C is the fastest one ($\mu_+ = 0.1$ $\mathrm{cm}^2\ \mathrm{V}^{-1}\ \mathrm{s}^{-1}$) measured for a calamitic mesogen.[11] In the crystalline phase, only a small photocurrent decay was observed. The hole mobilities show temperature-dependent nature in those mesophases, where they *gradually decrease* as the temperature is elevated, in contrast to the temperature-independent mobility of calamitic liquid crystalline semiconductors.[5,6] Additionally, any clear change of the mobility could not be seen at the phase transitions. However, it is reasonable to see such small changes in the XRD patterns at the phase transitions as described below. The typical decay curve observed indicates that the holes are mobile without any significant dispersion in spite of the polydomain film. Furthermore, the hole mobility does not depend on the electric field. This is similar behaviour to that of highly ordered smectic phases. For the negatively charged carriers, however, only a very small photocurrent decay was observed in all mesophases.

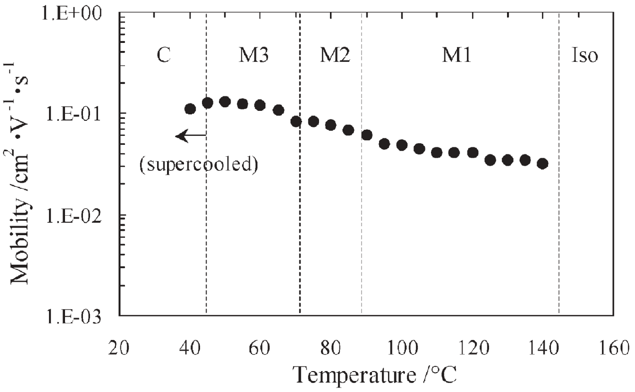

**Fig. 3** Mobility of positive carriers as a function of temperature under an electric field of $3 \times 10^4$ V $\mathrm{cm}^{-1}$ (sample thickness: 16.7 μm).

On the other hand, the XRD results (Fig. 4) indicate that these mesophases are three dimensional in nature. In the wide angle region, the broad halo around $2\theta$ = *ca.* 22° derived from the molten alkyl chains indicates that these phases are mesomorphic. The *d*-spacing ratio of the five reflections in the low angle region is 1 : 1/2 : 1/3 : 1/4 : 1/5, strongly indicating a smectic-like layered (lamellar) structure in these three phases. The (001) reflection at 32.9 Å correlates approximately to a full length of one molecule. A few sharp reflections detected in the wide angle region indicate the higher order of molecular packing within a layer. The assignment of all reflections obtained was carried out to reveal these three mesophases exhibit a three-dimensional order possessing a lamellar-type orientation of molecules (see, ESI†), suggesting a close arrangement of molecules within the layer.

The optical textures of these mesophases are shown with a lot of disclination lines in each domain of M3 phase in contrast to the homogeneous texture of the M1 phase (see, ESI†).

In the meantime, the symmetry of the 1,4-dithienylbenzene core ($C_{2h}$) is higher than the symmetry of liquid crystalline semiconductors reported so far,[5,6] such as $C_2$ -symmetry of 2-phenylnaphthalene, and $C_{2v}$ of terthiophene and is the same as that of quaterthiophene. The high symmetry of the 1,4-dithienylbenzene core is due to simple and good molecular design: two thiophene rings symmetrically attaching at 1,4-positions of a phenyl group. Therefore, such a fast mobility of carriers might be related to the molecular symmetry *via* closer packing of molecules.

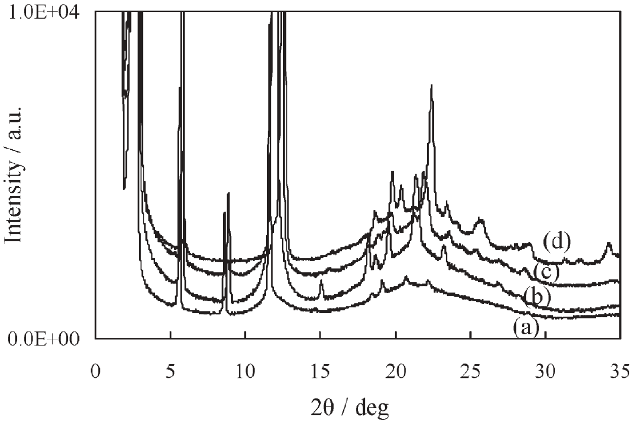

**Fig. 4** Temperature dependence of X-ray diffraction patterns (powder) of 8-TPT-8 (non-oriented) at (a) 120 °C (M1), (b) 75 °C (M2), (c) 60 °C (M3), (d) 30 °C in Cryst phase.

In summary, we have successfully found a novel thiophene/phenylene-based calamitic mesogen showing the fastest hole mobility in the highly ordered mesophases. Also it was indicated that the replacement of the central core in 3-ring systems of thiophene does not affect the charge transport properties, though giving a change of the mesomorphism. This indicates that a high carrier transport in calamitic liquid crystals can be achieved even if the $\pi$-conjugation system is not extended too much like in discotic liquid crystals[12] and implies the small modification of 3-ring systems of thiophene lead to the mesomorphism control without a drastic change of the mobility.‡

## Notes and references

‡ Selected data for 8-TPT-8: HRMS (EI, 70 eV) 466.2734 (calcd 466.2728 for $C_{30}H_{42}S_2$).; $^1$H-NMR (400 MHz, $CDCl_3$, TMS) $\delta$ 0.88 (t, $J$ = 7.1 Hz, 6H, $CH_2(CH_2)_6\mathit{CH_3}$), 1.28–1.39 (m, 20H, $CH_2CH_2$ $(\mathit{CH_2})_5CH_3$), 1.70 (m, 4H, $CH_2\mathit{CH_2}$ $(CH_2)_5CH_3$), 2.81 (t, $J$ = 7.1 Hz, 4H, $\mathit{CH_2}CH_2$ $(CH_2)_5CH_3$), 6.73 (d, $J$ = 3.4 Hz, 2H, thiophene-*H*), 7.12 (d, $J$ = 3.4 Hz, 2H, thiophene-*H*), 7.53 (s, 4H, benzene-*H*); $^{13}$C-NMR (400 MHz, $CDCl_3$) $\delta$ 14.10, 22.66, 29.13, 29.23, 29.34, 30.29, 31.66, 31.87, 122.51, 125.05, 125.71, 133.36, 141.25, 145.75; Elemental Analysis Calcd: C, 77.19; H, 9.07; S, 13.74. Found: C, 76.93; H, 9.33; S, 13.50.; $\lambda_{\mathrm{max,\ abs}}$ = 342 nm (log $\varepsilon$ 4.54), in chloroform; ICP-MS: Sn < 0.1 ppm

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10 The ICP-MS measurement and elemental analysis gave good agreement to the predicted ones. If the small amount of tin residue influences on the drift mobility, a significant low drift mobility should be observed, when it would work as the deep trap site of charged carriers.

11 Hole mobility $\mu$ was calculated from the equation, $\mu = d/t_\tau E$, where $d$ is the sample thickness and $E$ an electric field strength. The transit time $t_\tau$ of photogenerated holes was determined from an inflection point in a double logarithmic plot in the decay curve. For the photo-excitation of the cell, $N_2$-pulse laser ($\lambda$ = 337 nm, pulse width = 800 ps) was used.

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