Charge-transport in crystalline organic semiconductors with liquid crystalline order†

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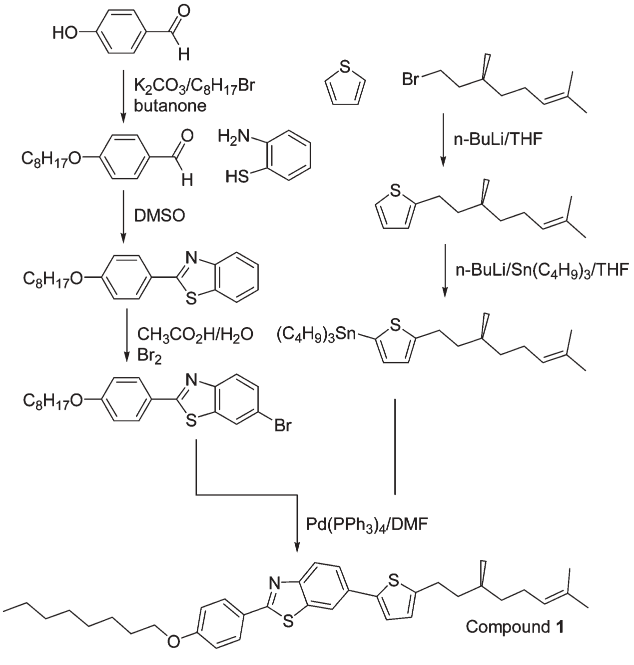
We report the design and synthesis of a liquid crystalline material exhibiting highly ordered smectic phases and high charge carrier-mobility; by a process known as "paramorphosis" highly ordered smectic phases can be transferred to the amorphous crystalline state on crystallisation without the formation of significant crystal grain boundaries and deep traps.

Conjugated polymers and oligomers have been investigated as organic semiconductors in thin film devices such as organic field effect transistors (OFETs)[1–6] and organic light-emitting diodes (OLEDs)[7–9] for almost two decades as an alternative to organic single crystals such as pentacene. More recently smectic liquid crystals have been shown to be a promising alternative approach to organic semiconductors.[10–13] Smectic liquid crystalline phases are self-assembling and self-annealing supramolecular assemblies that facilitate the formation of multidomain films with no physical grain boundaries between the small domains (>1 μm). The thin film then effectively resembles one large monodomain with no defects just like a single crystal. The layer structure present in all smectic liquid crystalline phases induces a high overlap integral of the characteristic long thin aromatic cores to facilitate hopping of charge carriers between them. The degree of order within different types of smectic phases has been shown to strongly influence the charge carrier mobility. The hole mobility is higher in the more ordered smectic E phase (1×10^{-2} cm^2 V^{-1} s^{-1}) with orthorhombic symmetry than in the less-ordered smectic B phase (1.6×10^{-3} cm^2 V^{-1} s^{-1}) with hexagonal symmetry, which in turn is higher than that in the smectic A phase (2.5×10^{-4} cm^2 V^{-1} s^{-1}) with no internal order within or between the layers.[10–13] The smectic E phase can be considered as a soft or plastic crystal with limited, cooperative rotational motion about the molecular long axis. This allows greater overlap of the wavefunctions of the molecular orbitals and facilitates charge carrier hopping.[12] However, the smectic phases of the organic semiconductors reported so far exist above room temperature and on cooling crystallisation occurs with the formation of large defects and crystal grain boundaries. These act as traps and lead to a significant reduction in carrier mobility and the total charge collected.[14,15] This severely limits the applicability of smectic liquid crystals in practical room temperature devices.

The aim of this paper is to demonstrate that the process of paramorphosis can be applied to the amorphous solid state of organic semiconductors formed on cooling from highly ordered smectic phases to resolve this problem. Paramorphosis often occurs when a smectic phase formed on cooling from another smectic phase exhibits the macroscopic organisation and therefore the optical texture of the smectic phase above it rather than its own more thermodynamically stable structure and textures as shown by optical microscopy. We designed and synthesised compound **1**‡ according to Scheme 1. The aromatic core is asymmetrical and non-linear in order to increase the viscosity. Long and branched terminal chains are present to further increase the viscosity and lower the melting point. The presence of a chiral centre should not to affect the charge carrier mobility in calamitic LCs.[13] The heterocyclic rings containing the electron-rich sulfur atom were chosen to contribute to a low ionisation potential and also induce a smectic phase. The aromatic core of compound **1** exhibits a flat molecular shape with very little inter-annular twisting due to the presence of fused heterocyclic rings and the thiophene ring. This shape facilitates a high degree of overlap of the molecular wave functions for an efficient hopping mechanism of charge transport.

The DSC trace shown in Fig. 1 shows that on heating crystals of compound **1** they melt first (Cryst–SmE = 75 °C) to form the



Scheme 1 Synthetic route to benzothiazole **1**.†

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† Electronic supplementary information (ESI) available: Experimental procedures and characterization data for the compounds shown in Scheme 1. See http://www.rsc.org/suppdata/cc/b5/b501875g/
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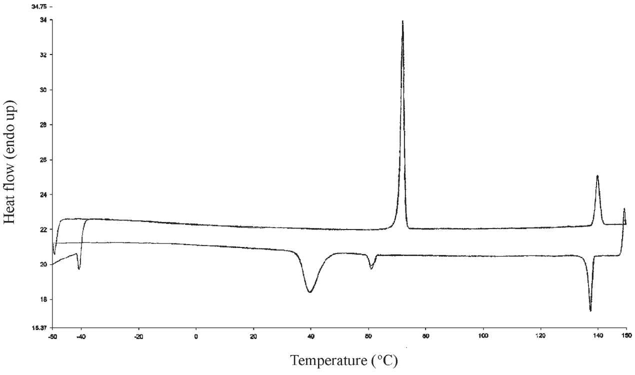

Fig. 1 Differential scanning calorimetry (DSC) scan for compound **1**.

smectic E phase and then a narrow smectic A phase (SmE–SmA = 143 °C) before clearing to form the isotropic liquid (SmA–I = 145 °C). The smectic A phase is reformed on cooling the isotropic liquid (I–SmA = 145°) followed by the formation of the smectic E phase (SmA–SmE = 143 °C). Hence the presence of two overlapping peaks. On further cooling a monotropic (unidentified) ordered smectic 3 phase is observed (SmE–Sm3 = 60 °C). Compound **1** then crystallizes to form an amorphous solid (Sm3–cryst ~ 40 °C) with the same melting point as the original crystal as shown by a second heating cycle. A glass transition temperature is not observed. This behaviour is reproducible through many heating and cooling cycles. The optical textures of the liquid crystalline phases of compound **1** viewed between crossed polarisers on cooling is shown in Fig. 2. The focal conic texture of the narrow smectic A phase (A) is transferred to the smectic E phase (B), then the ordered smectic 3 phase (C) and finally the amorphous crystalline state (D). These micrographs confirm that paramorphosis occurs on cooling. The short-range spatial order present in the small domains of the smectic phase as well as the overall macroscopic structure of the smectic film is transferred to the crystalline state of compound **1** with no formation of crystal grain boundaries, see Fig. 2(d). The dark disclination lines are domain walls representing changes in the director orientation and *not* physical defects such as those present in crystals as grain boundaries.

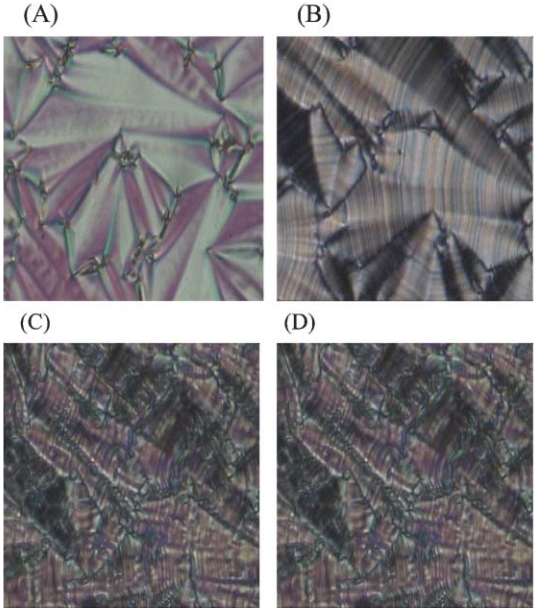

Fig. 2 Photomicrographs of compound **1** on cooling: (A) smectic A phase, (B) smectic E phase, (C) smectic 3 phase, (D) crystal phase.

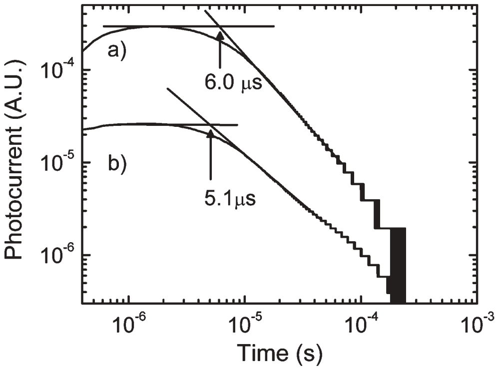

Fig. 3 Photocurrent transients for (a) holes and (b) electrons at 25 °C. The arrows indicate the transit times of carriers across the cell.

Fig. 3 shows the photocurrent [$I(t)$] transients for electrons and holes at 25 °C. The transients are somewhat dispersive and the photocurrent for holes is much greater than that for electrons. Fig. 4 shows the electron and hole mobilities as a function of temperature on cooling from the isotropic phase. The cell thickness was 2.3 μm and V = 12 V.§ For both carrier types, there is a discontinuity in the mobility values at the transition from the liquid to the smectic A phase. The temperature range of the smectic A phase is very narrow (2 °C) and a high degree of order is expected in the smectic A phase close to the transition to the smectic E phase due to pretransitional effects. This is evidenced by the overlapping peaks in the DSC trace, see Fig. 1. Therefore, the mobility is comparable in both phases due to a high induced order in the smectic A phase. A further discontinuity is observed for electrons at the smectic E to smectic 3 transition but, in this case, the mobility increases with increasing order. The hole mobility is approximately temperature independent in the smectic E phase and decreases sharply on approaching the smectic 3 phase. This is a commonly observed phenomenon for the mobility in smectic liquid crystals and is usually regarded as a characteristic feature of electronic transport in ordered organic materials.[10,11] It increases

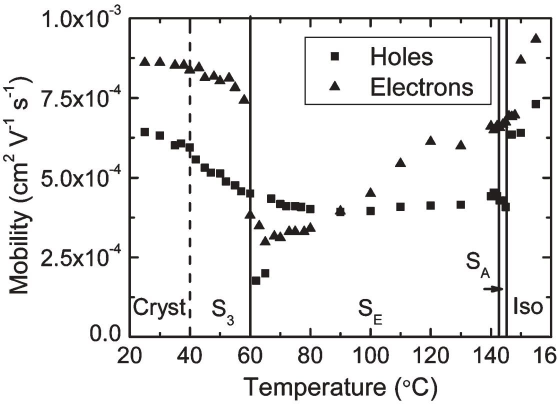

Fig. 4 Mobility of compound **1** as a function of temperature on cooling from the isotropic phase.

with decreasing temperature in the smectic 3 phase. For both carriers there is no change in transport characteristics on entering the amorphous crystalline phase from the soft crystalline smectic 3 phase. Similar trends in the carrier mobility *vs.* temperature are observed for both electrons and holes on heating but with a substantial degree of hysteresis; the discontinuities in the mobility values, which occur on entering the smectic E phase, are observed at 75 °C in accordance with the DSC data. These results confirm that paramorphosis results in the retention of high carrier mobilities in the crystal at room temperature and is in stark contrast to previous results on smectic organic semiconductors.[10–13]

The integral $I(t)\mathrm{d}t$ can be used as a measure of the total collected charge when the dielectric relaxation time is longer than the transit time.[16] The total collected charge of both electrons and holes does not change on crystallisation from the smectic 3 phase showing that there is no change in the quantum efficiency of photogeneration and no new bulk traps are formed by defects or grain boundaries. The charge generated by electrons is almost a factor of seven lower than that observed for holes, which implies that the compound has substantially more deep traps for electrons than holes.

In conclusion it appears apparent that the high degree of short-range order present in highly ordered smectic phases can be transferred by paramorphosis to the amorphous crystalline state on crystallisation *without* the formation of significant crystal grain boundaries and many deep traps. An ideal order for the manifestation of this phenomenon on cooling is a relatively fluid and disordered smectic A phase first for macroscopic alignment followed by the formation of ordered smectic phases with orthorhombic and hexagonal symmetry followed by the formation an amorphous solid with only short-range order and no crystal grain boundaries. These findings suggest that the high mobility of existing organic semiconductors could be further increased by modifying their chemical structure to induce the formation of highly ordered smectic phases.

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Notes and references

‡ 2-{5-[(*S*)-3,7-Dimethyloct-6-enyl]thiophen-2-yl}-5-(4-octyloxyphenyl)benzothiazole (compound **1**): A mixture of 6-bromo-2-(4-octyloxyphenyl)benzothiazole[14] (1.7 g, 0.0041 mol) 5-tributylstannyl-2-[(*S*)-3,7-dimethyloct-6-enyl]thiophene (2.29 g, 0.0045 mol) and tetrakis(triphenylphosphine)palladium(0) (0.23 g, 2.03 × 10^{-4} mol) in DMF (75 cm^3) was heated at 90 °C for 24 h. The mixture was allowed to cool to RT and the solution was treated with a saturated potassium fluoride solution (100 cm^3) to destroy the tin side products. DCM (2 × 200 cm^3) was added and the combined organic layers were washed with brine (4 × 200 cm^3), dried ($MgSO_4$), filtered and concentrated under reduced pressure. The crude product was purified by gravity column chromatography [silica gel, ethyl acetate–hexane, 10%:90%] to yield a white solid (1.31 g, 58%), which was further purified by preparative HPLC and recrystallisation from a DCM–ethanol solvent mixture. Purity: 99.9% (GC/HPLC). ^{1}H NMR ($CDCl_3$) δ_H: 0.89 (3H, t), 0.96 (3H, d), 1.16–1.40 (10H, m), 1.48 (2H, qnt), 1.56 (2H, qnt), 1.62 (3H, s), 1.69 (3H, s), 1.70–1.76 (1H, m), 1.82 (2H, qnt), 1.94–2.07 (2H, m), 2.76–2.88 (2H, m), 4.03 (2H, t), 5.11 (1H, t), 6.76 (1H, d, J = 3.6), 6.98 (2H, d, J = 8.7), 7.18 (1H, d, J = 3.6), 7.67 (1H, dd, J = 8.7, 1.7), 7.97 (2H, d, J = 8.7), 8.00–8.02 (2H, m). IR v_{max}/cm^{-1}: 3045, 2919, 2851, 1605, 1520, 1465, 1301, 1261, 1222, 1175, 1045, 998, 834, 817, 694, 561. MS (*m*/*z*): 559 (M$^+$, 100%), 474, 434, 322, 293.

§ *Device fabrication*: cells of thickness 1.5–10 μm were constructed by gluing two glass slides with patterned InSnO electrodes and separated with spacers. The cell thickness was measured using white-light transmission prior to filling. The cells were filled with compound **1** in its isotropic phase by vacuum-assisted capillary action and then sealed. Time-of-flight measurements were made using a conventional set-up.[17] The samples were excited with UV light from a nitrogen laser of wavelength 337 nm and a pulse width of 5 ns. The laser fluence was kept sufficiently low to avoid space-charge distortion of the applied electric field.

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