# Enhanced charge conduction in discotic liquid crystals

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At relatively low electric fields the conduction of thin films (2–6 μm) of the discotic liquid crystal (HAT6–PTP9) sandwiched between ITO electrodes and homeotropically aligned is low and is consistent with space-charge limited behaviour. However when annealed at high temperatures and electric fields the films undergo a transition and the electrical conductivity increases by up to 5–6 orders of magnitude. Studies show that this increase in the conductivity is not due to filament growth or to bulk molecular breakdown but rather to some chemical or physical change at the electrode surface.

The unique columnar architecture of discotic liquid crystals combined with their self-annealing properties and the ease with which they form bulk-aligned samples makes them attractive for a range of applications as 'one-dimensional' conductors.[1–3] Like other organic compounds, pure discotic liquid crystals are insulators. Charge can be injected from an electrode surface but typically there is a significant barrier (∼0.5 eV) to such charge-carrier injection and the liquid-like disorder of these materials means that carrier mobilities are also low ($4.4 \times 10^{-4}$ cm$^2$ V$^{-1}$ cm$^{-1}$ for holes in HAT6 in the Col$_h$ phase at 75 °C).[4–6] Charge-carrier hopping rates are typically $10^{10}$ Hz and the conductivity anisotropy (parallel *versus* that perpendicular to the columns) typically $10^3$.[7] Higher mobilities have been achieved by increasing the size of the aryl core of the discogen (0.46 cm$^2$ V$^{-1}$ cm$^{-1}$ for holes in the Col$_{h3}$ phase of alkyl substituted *peri*-hexabenzocoronenes at 192 °C) or by exploiting more-ordered phases such as the helical phase of 2,3,6,7,10,11-hexakis(hexylthio)triphenylene (HHTT $1 \times 10^{-2}$ cm$^2$ V$^{-1}$ cm$^{-1}$ at 65 °C), the plastic phase of HAT3 ($1.3 \times 10^{-2}$ cm$^2$ V$^{-1}$ cm$^{-1}$ at 25 °C) or the ordered 'CPI' (complementary polytopic interactions) system HAT6–PTP9 ($2.3 \times 10^{-2}$ cm$^2$ V$^{-1}$ cm$^{-1}$ at 120 °C).[8–10] As shown in Fig. 1, 1:1 mixtures of these two aromatic compounds give a Col$_h$ phase between 66 and 155 °C.[11–14] This readily supercools to room temperature and under these conditions recrystalisation is very slow.

In this report the *I–V* characteristics for the ITO/HAT6-PTP9/ITO system are investigated experimentally. At moderate temperatures and relatively low fields the systems show behaviour dominated by charge injection. However at high temperatures ($T > 180$ °C) there exists a critical field following which the system undergoes a transition and the conductivity increases by up to 5–6 orders of magnitude. In this state the threshold for charge injection (previously a major limiting factor for the conduction) appears to have been largely removed.[15]

The DC studies were made in ITO coated glass cells, manufactured by EHC Ltd. The electrodes were spaced at a distance of 2–6 μm by polyimide spacers and the electrode area was approximately 0.5 cm$^2$. Alternatively electrodes were made of Au and Al evaporated on glass spaced with PTFE film. The CPI mixture was heated into the isotropic phase and flowed into the cell *via* capillary action. *I–V* curves and all DC measurements were taken with a 6517 Keithley electrometer. The temperature of the sample was controlled using a Linkam TMS 91 temperature controller that was accurate to 0.1 K. Samples were aligned by being heated into the isotropic phase and slowly cooled into the columnar phase. Polarising microscopy showed the sample to be homeotropically aligned.

The *I–V* curve for the ITO coated cell as described above is shown in Fig. 2a, the measurements were taken at 135 °C with the sample being in the liquid crystal columnar phase. The results show typical behaviour for discotic liquid crystal systems.[4] The graph can be explained by splitting it up into two main regions, the highly resistive ohmic region at low fields and the space charge limited region at higher fields. In the low field regime Fig. 2a there is negligible conduction and also negligible charge carrier injection at the liquid crystal/electrode interface. In the higher field regime the ITO electrode acts as a hole injector and conduction is dominated by holes.[16] Although electron–hole creation may be the preferred route for conduction, at room temperature the charge carriers will not have enough energy to overcome the potential barrier at the electrode/liquid crystal interface. Therefore, a potential has to be applied to reduce the barrier at this interface and to increase the conduction. In the higher field region the curve
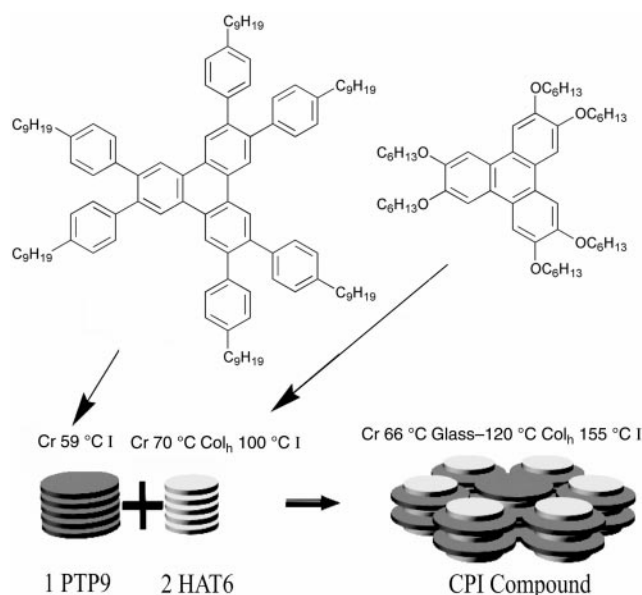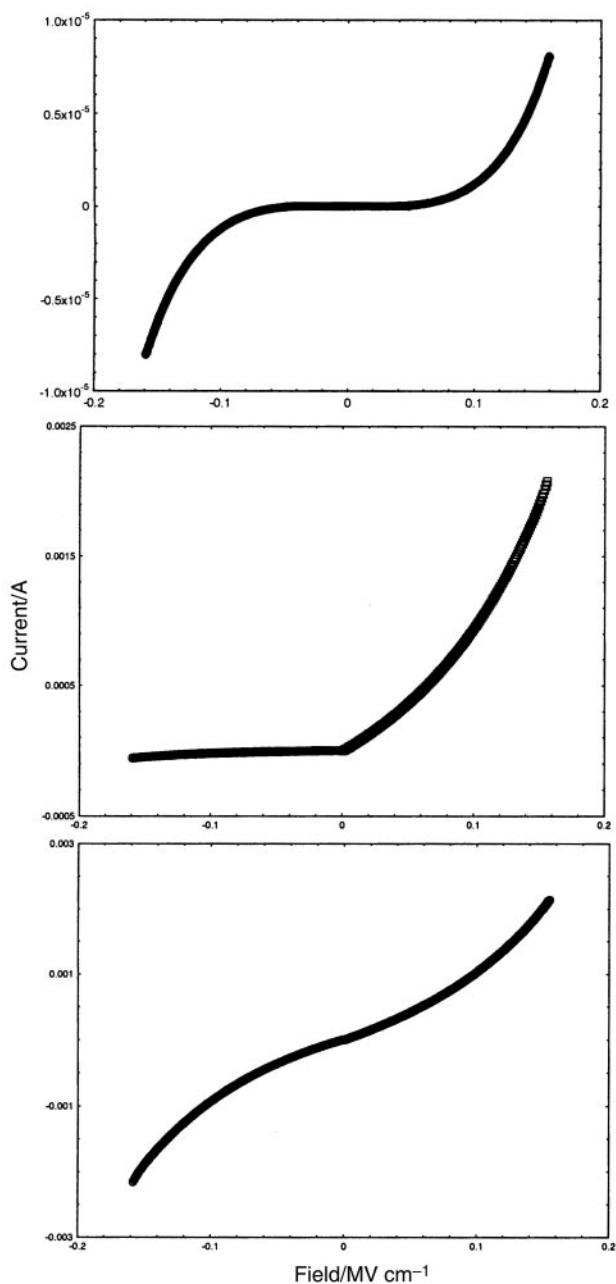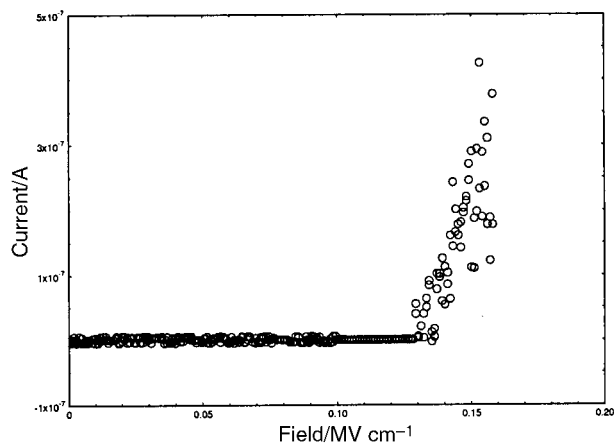


**Fig. 1** Columnar stacking in the 1:1 complex of HAT6 (**1**) and PTP9 (**2**). Diagram shows addition of two complementary disk shaped molecules giving rise to the alternating structure of CPI liquid crystal (Cr 66 °C, Col$_h$ 155 °C, I).

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**Fig. 3** Current–voltage curve showing the onset of the high conduction at high fields. The initial flat portion of the curve has behaviour consistent with that in Fig. 2a.

field annealing procedure is now repeated with a reversed polarity the symmetric current–voltage plot shown in Fig. 2c can be obtained. This behaviour clearly shows that the enhancement is due to some modification of the interface, and it is not consistent with the hypothesis of filament growth or molecular breakdown within the bulk of the sample.

Similar enhancements of the conductivity have been observed in HAT6, 1-fluoro-HAT6 and 1-nitro-HAT6. Measurements have been taken using Al and Au electrodes and they also show the enhancement behaviour. The HAT6–PTP9 mixtures take several days to crystallize, but upon crystallizing the high conduction is lost and the sample requires 'field annealing' again to restore the high conduction.

One means of assessing the origin of the field-annealed conductivity enhancement is to apply a DC electric field and measure the current flow as a function of time. If the enhancement is due to the creation of long-lived ions within the sample then, over time, charged particles will flow to the electrodes forming a resistive layer. This will lead to the current decreasing with time as the double layer prevents charge reaching the electrodes. Time dependent conduction measurements were taken for the field-annealed sample. A decrease in the current with time was observed and the current decayed by a factor of 3 to a constant value. This shows that there are ions present but that it is not this process that is dominant when considering the conductivity enhancement.

The origin of the enhanced conductivity in the 'field-annealed' ITO/HAT6-PTP9/ITO system is not yet clear but some possible explanations can be ruled out. Firstly, it is not the result of filamentous growth from the electrode surface. This is unlikely in view of the fact that similar behaviour is observed not only for ITO but also Au and Al electrodes. Furthermore it can be positively discounted on the basis of the observed rectification behaviour (Fig. 2). The last observation also shows that it is not the result of chemical decomposition in the bulk of the sample leading to ionic products. Indeed the rectification shows that this is a result of changes at the interface rather than in the bulk. Whether this change is chemical (*e.g.* deposition of a polymer layer) or physical (*e.g.* improved alignment of the surface layer or self doping) is not entirely clear but the latter explanation seems more likely in view of the observation that the enhanced conduction behaviour disappears in samples that are allowed to crystallise and is only re-established when the sample is once again heated into the $Col_h$ phase and re-annealed at high fields.

Whatever the explanation the practical significance is considerable and this discovery should prove important to all attempting to develop applications of discotic liquid crystals.



**Fig. 2** a). *I–V* response for ITO/HAT6-PTP9/ITO cells spaced at 6 μm, at 135 °C in the liquid crystal columnar phase. The central flat portion of the graph arises because of the mismatch of work functions between the liquid crystal and the electrode at the interface. The current then exhibits a $V^2$ dependence indicative of space charge injection. b). *I–V* response of an equivalent cell at 135 °C showing the enhanced conduction following high field annealing of the sample in one direction. c). *I–V* response of the same cell at 135 °C after high field annealing with a reversed polarity. The rectification apparent in (b) is now lost.

shows a $V^2$ dependence due to charge injection limited behaviour.[17] However, if the system is heated into the isotropic phase (190 °C) and a field applied there is a critical field at which the conduction increases by up to 5–6 orders of magnitude, this high value is maintained even after the field and elevated temperature are removed. Fig. 3 shows the onset of the enhancement of the conductivity.

Fig. 2b shows the *I–V* curve for a sample taken directly after this high field annealing. For equivalent fields the conductivity has increased from the microamp to the milliamp regime and the *I–V* curve shows a much weaker dependence on space charge injection. The enhanced conductivity systems also exhibit rectification behaviour (Fig. 2b). However, if the high

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## Notes and references

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