First Observation of an n-Doped Quasi-One-Dimensional Electronically-Conducting Discotic Liquid Crystal

Neville Boden,* Ruth C. Borner, Richard J. Bushby, and Jonathan Clements

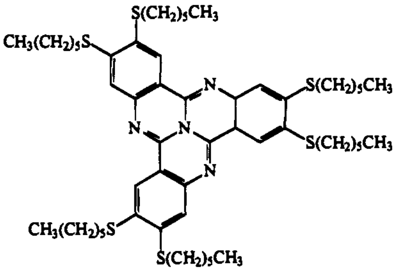
Centre for Self-Organising Molecular Systems
The University of Leeds, Leeds LS2 9JT, U.K

Received June 27, 1994

We describe herein the first reported example of an n-doped, discotic-liquid-crystalline quasi-one-dimensional semiconductor.

There is currently considerable interest in the preparation of p-doped electronically conducting discotic liquid crystals,[1−5] in which the charge carriers are essentially confined to the molecular columns. For example, when 2,3,6,7,10,11-hexakis(hexyloxy)triphenylene (HAT6) is doped with 1 mol % of the electron acceptor $AlCl_3$, the conductivity σ increases from the undoped value of less than 10^{-9} S m^{-1} to approximately 10^{-3} S m^{-1}. In essence, the $AlCl_3$ extracts an electron from the triphenylene ring of HAT6 to produce a positive hole. The migration of charge along the stacks of triphenylene cores gives rise to a conductivity $\sigma_{\parallel}$. This is some 3 orders of magnitude greater than the value measured in the perpendicular direction $\sigma_{\perp}$.[6,7]

The principle of doping to produce discotic-liquid-crystalline conductors is expected to be quite general and should be extendible, therefore, to doping with electron donors. Doping with electron acceptors ideally requires discotic liquid crystals with low oxidation potentials,[8] for example, π-rich systems such as the alkoxy-substituted triphenylenes. On the other hand, doping with electron donors requires discotic liquid crystals with low reduction potentials, for example, the π-deficient system 2,3,7,8,12,13-hexakis(hexylthio)tricycloquinazoline, (HHTQ, **1**).



1

This principle is illustrated by the effects of doping HHTQ with potassium metal, an electron donor:

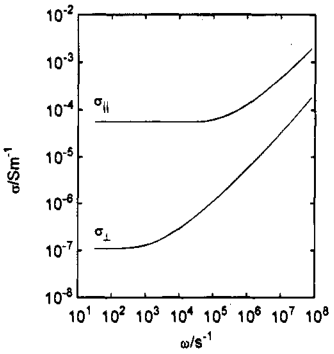


Figure 1. Ac conductivity of 2,3,7,8,12,13-hexakis(hexylthio)tricycloquinazoline, **1**, doped with 6 mol % of potassium metal in the liquid-crystalline phase, D_h, at 464 K in the frequency range 5 Hz to 13 MHz.

$$\mathrm{HHTQ} + \mathrm{K} \rightarrow \mathrm{HHTQ}^{\bullet -}$$

HHTQ[9] was synthesized by the method of Keinan et al.[10] Doping was effected by mixing HHTQ with 6 mol % of potassium metal in vacuo. The phase behavior of the doped material was established by DSC to be

$$\mathrm{K}\ (349.5{-}347\ \mathrm{K})\ \mathrm{D_h}\ (484.5{-}483\ \mathrm{K})\ \mathrm{I}$$

where K, D_h, and I represent the crystalline, hexagonal discotic, and isotropic phases, respectively. This is to be compared with that of undoped HHTQ,

$$\mathrm{K}\ (351\ \mathrm{K})\ \mathrm{D_h}\ (486\ \mathrm{K})\ \mathrm{I}$$

The effect of the dopant is, therefore, to depress the transition temperatures slightly and to separate the phases by biphasic regions.

Samples were sealed in glass tubes and ultrasonicated at 338 K for 48 h to ensure complete reaction and homogeneous dispersion of the product. The sample tubes were opened (in a drybox under an atmosphere of N_2[11]) and the conductivity cells filled.

Ac conductivity measurements were made over the frequency range 5 Hz to 13 MHz with a Hewlett-Packard 4129 LF impedance analyzer using a four terminal pair electrode configuration with samples approximately 200 μm thick. The temperature of the sample was controlled using an N_2 gas-flow system and an Oxford Instruments temperature controller and measured using copper/constantan thermocouples and a Keithley 181 nanovoltmeter. Aligned samples were produced by cooling at 3 K/min from the isotropic phase (488 K) into the mesophase (478 K) in the presence of a magnetic field (2.2 T).[7] Because of the diamagnetic anisotropy of the mesogen, this produces a material in which there is a two-dimensional distribution of column directors perpendicular to the magnetic field.[12] Therefore, by measuring the conductivity parallel and perpendicular to the applied field, we are thus able to derive values for both $\sigma_{\parallel}$ and $\sigma_{\perp}$.[7]

Figure 1 shows the frequency dependence of $\sigma_{\parallel}$ and $\sigma_{\perp}$ in the D_h mesophase of HHTQ. In unaligned samples of HAT6/$AlCl_3$ the conductivity behavior is dominated by frozen-in defect structures.[7] As Figure 1 confirms, this is not the case for aligned samples.[7] For both $\sigma_{\parallel}$ and $\sigma_{\perp}$, an $\omega^{0.8}$ frequency dependence is found at higher frequencies. At lower frequencies, $\sigma \sim \omega^0$. This type of behavior is characteristic of dispersive transport.[13]

---

(1) Chiang, L. Y.; Stokes, J. P.; Safinya, C. R.; Bloch, A. N. *Mol. Cryst. Liq. Cryst.* **1985**, *125*, 279−288.

(2) Piechocki, C.; Simon, J.; Skoulios, A.; Guillon, D.; Weber, P. *J. Am. Chem. Soc.* **1982**, *104*, 5245−5427. Belarbi, Z.; Maitrot, M.; Ohta, K.; Simon, J.; André, J. J.; Petit, P. *Chem. Phys. Lett.* **1988**, *143*, 400−403. Belarbi, Z.; Sirlin, C.; Simon, J.; Andre, J. J. *J. Phys. Chem.* **1989**, *93*, 8105−8110.

(3) van Keulen, J.; Warmerdam, T. W.; Nolte, R. J. M.; Drenth, W. *Recl. Trav. Chim. Pays-Bas* **1987**, *106*, 534−536.

(4) Gregg, B. A.; Fox, M. A.; Bard, A. J. *J. Am. Chem. Soc.* **1989**, *111*, 3024−3029. Schouten, P. G.; Warman, J. M.; de Haas, M. P.; Fox, M. A.; Pan, H.-L. *Nature* **1991**, *353*, 736−737.

(5) Vaughan, G. B. M.; Heiney, P. A.; McCauley, J. P., Jr.; Smith, A. B., III. *Phys. Rev. B* **1992**, *46*, 2787−2791.

(6) Boden, N.; Bushby, R. J.; Clements, J.; Jesudason, M. V.; Knowles, P. F.; Williams, G. *Chem. Phys. Lett.* **1988**, *152*, 94−99; **1989**, *154*, 613.

(7) Boden, N.; Bushby, R. J.; Clements, J. *J. Chem. Phys.* **1993**, *98*, 5920−5931. Boden, N.; Bushby, R. J.; Clements, J. *J. Mater. Sci.: Mater. Electron.* **1994**, *5*, 83−88.

(8) Pope, M.; Swenberg, C. E. *Electronic Processes in Organic Crystals*; Clarendon Press: Oxford, 1982.

(9) Lit. K (367.9 K) D_h (486.6K) I.

(10) Keinan, E.; Kumar, S.; Singh, S. P.; Ghirlondos, R.; Wachtel, E. J. *Liq. Cryst.* **1992**, *11*, 157−173.

(11) H_2O, <10 ppm; O_2, <5 ppm.

(12) Goldfarb, D.; Luz, Z.; Zimmerman, H. *J. Phys.* **1981**, *42*, 1303.

(13) Scher, H.; Montroll, E. W. *Phys. Rev. B* **1975**, *12*, 2455.

0002-7863/94/1516-10807$04.50/0

Table 1. Summary of Conductivity Results for HHTQ Doped with 6 mol % Potassium and Comparison with Equivalent Sample of HAT6 Doped with 5 mol % $AlCl_3$[a]

	HHTQ/K	HAT6/$AlCl_3$
charge carrier density/m^3	7.0×10^{22}	2.6×10^{25}
$\sigma_{\|}/(S\ m^{-1})$	2.9×10^{-5}	5.0×10^{-2}
anisotropy $\sigma_{\|}/\sigma_{\perp}$	518	939
mobility $\mu_{\|}/(m^2\ V^{-1}\ s^{-1})$	2.5×10^{-9}	1.2×10^{-8}
hopping time τ/s	7.8×10^{-10}	1.6×10^{-10}

[a] All results are at 360 K in the respective mesophases.

Table 1 compares some of the data for HHTQ/K and HAT6/$AlCl_3$ at comparable levels of dopant and temperature. Charge carrier densities n have been determined by double integration of ESR signals.[6,7,14] Extensive measurements of spin concentrations and corresponding conductivities in both of these materials have shown that spin concentrations can be identified with charge carrier densities, and that the carriers are independent and singly charged.

Charge carrier mobilities $\mu_{\|}$ parallel to the columns have been estimated using $\sigma_{\|} = ne\mu_{\|}$, where e is the electronic charge and $\sigma_{\|}$ is the low-frequency limiting conductivity. The values are summarized in Table 1. We see that the carrier mobilities in both HHTQ/K and HAT6/$AlCl_3$ are very much lower than the minimum values associated with band-like transport in molecular solids,[15] $\mu \sim 10^{-4}\ m^2\ V^{-1}\ s^{-1}$. They are more consistent with a transport mechanism involving a hopping of carriers between neighboring molecules along the columns. These mobilities are apparently 1−2 orders of magnitude lower than those determined by pulsed radiolysis time-resolved microwave conductivity in liquid−crystalline phthalocyanines,[16] but this may only reflect the high frequency at which the latter measurements were made.

A hopping mechanism is more in keeping with the intrinsic liquid-like disorder in the columnar organization in discotic liquid crystals. The frequency dependence of the conductivity parallel to the columns in HHTQ can therefore be understood in terms of the hopping of electrons between neighboring molecules. Since the probability of an electron hop between adjacent molecules is an exponential function of their separation, the intrinsic liquid-like disorder[17] in the columnar packing, as well as the distribution of intermolecular separations which results, leads to a distribution of transition rates. The transport properties of the system are then completely dominated by this distribution.[18] The $\omega^{0.8}$ dependence of σ at high frequencies arises as a consequence of this distribution, while the ω^0 dependence at low frequencies is determined by the lowest transition rate for hopping. The hopping time τ for this process can be estimated from[8]

$$\tau = \frac{ed^2}{2kT\mu_{\|}}$$

where d is the average intermolecular separation ($d \sim 0.35$ nm) and T is the absolute temperature. Values of τ estimated in this way are shown in Table 1. The similarity in the values for both HHTQ and HAT6 indicates that charge carriers migrate along the molecular columns in these discotic liquid crystals by a similar mechanism. The mechanism of conductivity perpendicular to the columns is less clear, but it is surprising that the mobilities are relatively high in view of the insulating liquid hydrocarbon nature of the matrix separating the columns of aromatic cores. Further studies are underway to establish whether or not these measurements reflect the intrinsic behavior or are a consequence of the defect structure of the samples.

In summary, it is now possible to prepare both p-doped and n-doped quasi-one-dimensional semiconducting discotic liquid crystals. Highly directional charge transport over large distances in discotic liquid crystals is therefore practicable. This property underpins possible future applications of discotic liquid crystals.

---

(14) Whereas in HAT6/$AlCl_3$ the spin concentration is almost stoichiometric, in the case of HHTQ/K the stoichiometry is variable, although the charge carrier mobilities are reproducible.

(15) Simon, J.; André, J. J. *Molecular Semiconductors*; Springer-Verlag: Berlin, 1985.

(16) Schouten, P. G.; Warman, J. M.; de Haas, M. P.; van der Pol, J. F.; Zwikker, J. W. *J. Am. Chem. Soc.* **1992**, *114*, 9028−9034.

(17) Safinya, C. R.; Clark, N. A.; Liang, K. S.; Varady, W. A.; Chiang, L. Y. *Mol. Cryst. Liq. Cryst.* **1985**, *123*, 205.

(18) Bernasconi, J.; Schneider, W. R.; Wyss, W. *Z. Phys. B* **1980**, *37*, 175−184. Alexander, S.; Bernasconi, J.; Schneider, W. R.; Orbach, R. *Rev. Mod. Phys.* **1981**, *53*, 175−198.