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Device applications of charge transport in discotic liquid crystals

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We discuss some of the unique structural and electronic properties of discotic liquid crystals, particularly the nature of the 'band structure', and of charge injection from metal electrodes. Attempts have been made to use conducting discotic liquid crystals in electroluminescent devices and in gas sensors. The latter are created by spin-coating a thin film of discotic liquid crystals onto an array of interdigitated electrodes. We discuss the temperature dependence of the conductivity of these new systems, analyse the mechanism of charge diffusion and the effect of adsorbed gases.

I Introduction

The columnar (Col) phases of discotic liquid crystals like the hexaalkoxytriphenylenes (HATn) are comprised of disordered stacks of disc-like molecules which are arranged on a regular two-dimensional lattice (Fig. 1).[1] Typically these materials also exhibit a crystalline (K) phase at lower temperatures and an isotropic (I) phase at higher temperatures. There are some, like the polymeric discotic compounds, which also have at least one low temperature glassy columnar phase.[2,3] Understanding the structure and the molecular dynamics of these materials is not a trivial task, and it is only now that molecular dynamical studies are beginning to give what appears to be a reasonably accurate description. These simulations also give the pair correlation functions in the different spatial directions and their temperature dependence.[4] Fig. 3 in reference 4 shows a computer simulation picture of a discotic phase using the Gay–Berne approach. These computer images are close to the way we imagine these systems to be based on X-ray and other structural data. At some stage the Gay–Berne potential will probably have to be improved by allowing higher order interaction effects to come into play. The important ones appear to be the quadrupolar core–core interactions.[5] X-ray data provide us with lattice constants and also give us estimates of fluctuations in the molecular order.[6] Dielectric,[7] ellipsometry,[8] electron diffraction[9] and optical microscopy studies have been carried out on a number of HAT-based discogens and the authors have been able to deduce dielectric anisotropy, dipolar relaxation rates and the temperature dependence of the order parameters. Within the framework of optical characterisation methods and with the criteria used in polarisation microscopy, it seems as if it is not too difficult to obtain aligned columnar liquid crystalline phases. More recently, it was discovered that discotic columns can also carry electric charge with relatively high mobilities μ, in the range $10^{-4} < \mu < 10^{-2}$ cm^2 V^{-1} s^{-1}.[10–13] The long time mobilities are highest when the material is in the columnar phase. This seems to imply that we have well defined energy bands in the columnar direction along which the carriers move and that this is true even in the highly dynamic liquid crystalline phases!

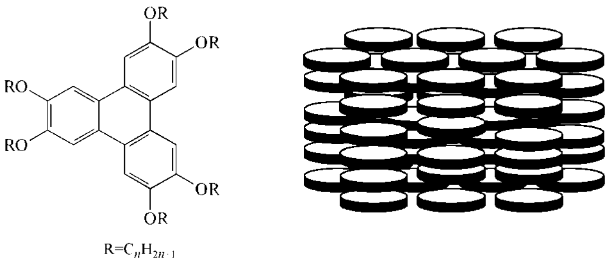

Fig. 1 Molecular structure of a typical triphenylene-based discogen, HATn (left) and a schematic representation of the columnar phase (right).

II Band structure

To examine how such 'molecular wires' arise we need to re-examine the concept of a band structure in a columnar array of discotic molecules. Indeed we need to ask 'if there is such a thing as a Bloch band structure'? The answer must be, 'no' in the simple one particle sense of the term, but 'yes' in the many body sense of the term! In HATn, for example, we have a HOMO–LUMO gap which is ~4 eV or more. In the phthalocyanine based discotic liquid crystals the band gap is lower, ~2.5 eV. The binding between molecules is in most cases mainly due to van der Waals forces. Direct electronic wave function overlap from one molecule into the positive core of a neighbouring molecule in the ground state is very weak. The positive core of the neighbour is well screened in the ground state and the orbitals extend only to roughly 1.5 Å out of the plane. Electronic banding processes are more complex than usual. Starting from the neutral state, consider an electronic charge fluctuation which originates on a single molecule, creating momentarily an exciton. This can also virtually split up, for example with the negative charges moving into a neighbouring molecule's LUMO leaving behind the positive partner charge. Such quantum charge fluctuations, in which pairs are excited and carriers separate into more or less strongly bound pairs, can take place on short time scales $\sim 3 \times 10^{-15}$ s. The virtual charges or excitonic pairs move along the columns and from column to column and in this way, by taking up more configuration space, they lower their kinetic energy. In other words by virtue of the fact that they can move around, the cost in energy in creating them is lowered. This is what one normally understands by electronic banding: lowering the single particle energy by allowing it to visit the other available sites in the lattice. Unlike a covalent semiconductor, however, the gain in kinetic energy from such single particle banding excursions in a discotic liquid crystal (typically ~0.4 to 0.8 eV) is small in comparison to the energy needed to separate the initially strongly bound electron-hole pair. The pair in a discotic liquid crystal is strongly bound by nearest neighbour Coulomb energies (~2.5–4 eV). Once created, the quantum pair will normally recombine geminately on a very fast time scale giving us a material with very low polarisability. In a covalently bonded material like silicon, on the other hand, the gain in banding energy is ~4 eV and far outweighs the cost in Coulomb energy of making visits onto the other atoms in the lattice so that here one can truly speak of well defined one particle energy bands. The short lived charge fluctuations and quantum excursions in a discotic column give only a small contribution to the binding energy with neighbours. However, energy bands can be generated by cooperative interactions (for example in the excited state) but by definition they are not single particle-like. UV absorption spectra confirm this point of view. They show us that the banding effects in the condensed state of such materials give rise to a shift in the main absorption peaks which is no more than about ~0.2 to 0.3 eV. This type of energy shift is in the range allowed by pair transfer mechanisms.[14]

When a real charge is introduced (injection of an electron), the situation is quite different. An extra charge in the LUMO band is much more weakly bound and the wave function is therefore more extended in space. This gives it a better overlap with the screened potential of the neighbours. The overlap to the nearest neighbour is strongly enhanced because the net charge induces a dipole in the two nearest neighbours thereby generating an extra energy $-\alpha_s\,[e^2/4\pi\varepsilon_o a^2]^2$ which is ~1 eV (α_s is the polarisability in the direction of the short axis and $\sim 26\times10^{-40}$ Fm[2,7] and a is the lattice distance in the stack ~3.5 Å). The induced image generates a potential for the electron to transfer into. It also provides a bias field that promotes tunnelling resonance transfer into the neighbours. The induced charge–polarisation interaction is the same for holes as it is for electrons. For electrons, however, the negative charge still sees a highly screened neighbour. In the case of holes the situation is quite different. The hole is a net positive charge that attracts the outer shell negative charges of its neighbours into itself. Electrons can jump into the hole by the usual tight–binding resonance step and they see the full Coulomb potential. This is clearly not so for electrons that only see the relatively weak induced interaction. There is evidently an asymmetry between electron and hole banding and consequently, contrary to simple intuition, the energy bands cannot have the same width. We expect the hole band to be somewhat larger with the resonance integral t_h ~0.2 eV giving a maximum band width ~0.8 eV. By way of contrast, for electrons, we expect t_e ~0.1 eV giving a maximum band width ~0.4 eV.[14]

The polarisation induced by the charged molecule is a strong function of the distance between the molecules. The coupling makes a strong electronic-lattice polaron. However, we can see that the liquid like oscillations along the column allow the dressed carrier to move quite efficiently from disc to disc along the stack at high temperatures. In the plane of the core where the charge is resident, one can also expect a polaronic relaxation which lowers the polaron transfer efficiency to the next molecule. Again this is apparently not observed at high temperatures.[11,13] Our estimates suggest that at low temperatures, polaron self-trapping must be important in discotic liquid crystals. However, to our knowledge, no one has yet seriously looked for polaronic renormalisation phenomena in discotic liquid crystals. This is probably because most researchers in this field are only interested in temperature ranges in which these materials are actually in the liquid crystalline phase and this means in practice temperatures which are quite high on the scale of self-trapping energies. In fact one only observes weakly dispersive transits with well defined charge mobilities in the liquid crystal phases.[13] The reason is that in this phase, the molecular structure is liquid like and self-repairs on a time scale of $\sim 10^{-5}$ s.[15] To our knowledge, there is no direct experimental evidence for polaronic lattice distortions in the liquid crystalline phases. To observe polaronic self-trapping energies, one probably has to go to low temperatures where the molecular motion freezes in and the mobility becomes strongly temperature dependent.[12] The time-of-flight measurements of Adam *et al.* on HATn go down to 70 K. The measured mobility is indeed strongly temperature dependent at low T. However, even from the data provided by these authors, one cannot deduce the existence of a strictly polaronic self-trapping energy. The effect, if any, is masked by the disorder fluctuations in the polarisation energy. This is specially true in dipole carrying molecules,[16] where one can unambiguously identify the signature of the dipolar disorder effect both in the time (dispersive transport) and in the steady state domain (Gaussian temperature dependent mobilities).[16] To see polarons, we need to study the low temperature transport properties, in particular the region below 100 K, with more care and more accuracy using dipole free mesogens. A polaron mobility should for example behave as eqn. (1).

$$\mu(T) \sim \nu \exp\left[-(T_0/T)^2\right] \exp\left[-E_p/kT\right] \qquad (1)$$

The first factor is typical for materials with Gaussian disorder of the polarisation energy.[15] The second and activated factor, is the polaronic self-trapping term[16] in which E_p is the polaron energy. This quantity will strongly depend on the type of discotic. It will be interesting to test this prediction against measurement at low temperatures.

III Charge injection and electroluminescence

When the molecular cores are in contact with a metal surface, depending on the way the molecule has been deposited, there can be a more or less strong electronic coupling between the π electrons on the conjugated core and the s-electrons on the metal surface. Under normal deposition (*e.g.* spin-coating) the coupling is expected to be fairly weak and we expect only physisorption to take place. For HATn, the Fermi level of a metal like gold or ITO will be roughly 1 eV above the valence band of the molecular columns. Charge cannot easily flow in and out, and ohmic conduction can only occur because there are defects in the material and ionic charge complexes which provide bridges for the charges to move between the electrodes and the electronic bands of the organic film. Even at low voltages, some charge always penetrates into the film and this phenomenon, known as electrode polarisation, masks the true bulk dielectric behaviour of the material. This is a problem if, for example, one measures the capacitance using direct metal–metal contacts to the organic film. As well as electrode polarisation, metal contacts also allow thermionic exchange of charge with the molecular bands, and this gives rise to a strongly temperature dependent dark current,[17] where in principle we should only see a weak dependence on temperature coming from the mobility.[11,13] Thermal charge injection and electrode polarisation can be demonstrated by comparing metallic cells with cells in which the metal is covered by an insulating layer. Fig. 2 illustrates the ac conductance in a cell in which the metal is covered by a very thin SiOx layer. The observed weak temperature dependence, which characterises the bulk transport, should be compared to the data taken with metal cells and shown in Fig. 3 of reference 17.

At high voltages it is possible to inject charge from metal electrodes into the valence band by average fields which are of order 10^5 V cm^{-1} or more. The tunnel distances for charges near the interface are ~10 Å. This still gives a small field heating. In fact the field at the interface barrier is much higher than the average field because there is always a small amount of charge in the material; enough to generate a space charge layer. The value of $\sim 10^5$ V cm^{-1} suffices for hole injection in triphenylene with ITO. To obtain electron injection, one needs low work function metals such as aluminium and calcium or one has to go to even higher average fields.

One potential application of discotic liquid crystals which is under active investigation is as an alternative to materials such as poly(phenylenevinylene) in electroluminescent displays.[18,19] Ideally, to obtain strong electroluminescence, we want to have both electron and hole injection using low and high work function contacts. Injected carriers of opposite

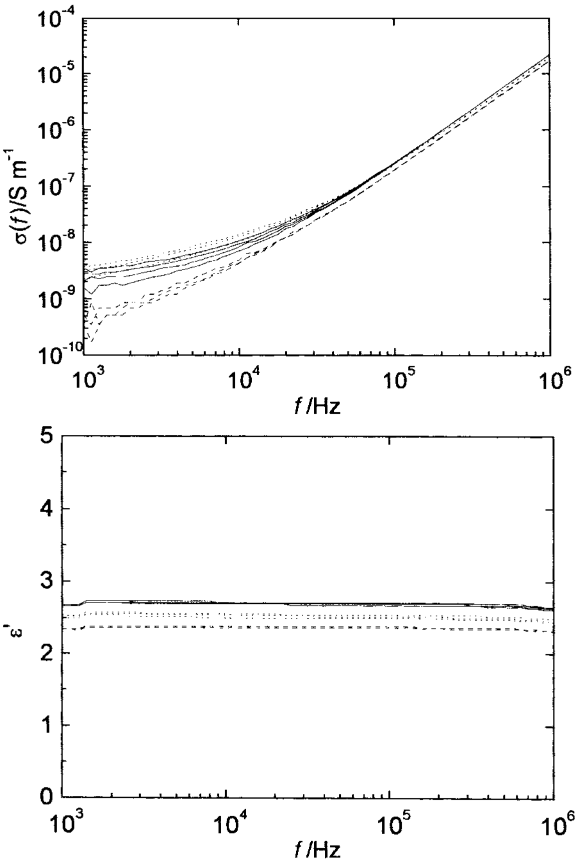

Fig. 2 (Top) The ac conductance of HAT6 (2,3,6,7,10,11-hexahexyloxytriphenylene) as a function of temperature and frequency and (Bottom) the real part of the dielectric permittivity measured for a thin film in a cell with SiOx insulated ITO electrodes. - - - - -(crystal, 310, 320, 330 K), ——(columnar, 340, 350, 360, 370 K), ...(isotropic phase, 380, 390, 400 K).

polarity will then move toward each other along the columns, combine and emit light.[20] In order to achieve double injection of electrons and holes and high enough luminescence, one needs high currents $j > 1$ mA and high fields $F > 10^6$ V cm^{-1}. These are close to break down fields for the HATn discotics which are $\sim 4.10^6$ V cm^{-1},[17] and this implies that long term stability of such devices is likely to be a serious problem. Ideally one would need an electron injector which is close to the LUMO band, but this is in practice very difficult to find. Hole injectors near the valence band are easier to find. This is because the work functions of discotic liquid crystals are in the range 5–6 eV; good for hole injection from metals such as ITO, gold and platinum, but not ideal for electron injection because the band gaps are relatively large. The other condition for long time stability is that the transport path in the film is very short so that only a small amount of heat is dissipated before the carriers meet. Since we are dealing with hopping conduction there is a phonon emitted at practically every hopping step. The resulting inelastic 'low mobility' implies that there is strong Joule heating and consequently an early breakdown of the device. One-dimensionality only makes things worse because a single defect holds up all the other carriers moving on the same column. One has to use thin films of maximum thickness $\sim$300 Å and this is indeed what Haarer and co-workers are using in their latest devices.[18]

Charge injection implies a non-linear voltage dependence of the currents. If the Fermi level lies in the conduction or valence bands, we have the classical 'space charge limited current' limit with the characteristic V^2 law known as Child's law.[21] If we have a barrier at the interface, the metal Fermi level is in the gap of the organic, as is usually the case with discotics. We then have a tunnelling law at low T which changes into an exponential voltage activated law at high T.[17] This has indeed been observed experimentally by several groups.[17–19] Using both X-ray and high voltage injection, Wendorff *et al.*[19] were able to show that deposited layers on metal surfaces can be annealed to form highly ordered columns with optimum charge injection efficiencies. As observed many times before, the alignment achieved in the liquid crystalline phase is so good that one can see almost perfect Gaussian charge transits.[11] Trapping occurs mainly at the interfaces to the electrodes.

IV The free surface and its effect on charge transport

The free surfaces of liquid crystals are fascinating objects. Large complex molecules are strongly hindered in their degrees of freedom when they are assembled into solids or liquid crystals. As a result one can expect the extra degrees of freedom near the surface where the absence of interacting neighbours should give rise to new and exciting ordering phenomena. For example, pre-ordering transitions at surfaces are observed for smectic liquid crystals and have been studied using ellipsometry and X-ray diffraction.[22,23] In smectics the ratio of inter- to intra-layer distances is such that the absence of neighbours on one side actually shields the system from large amplitude fluctuation modes and encourages crystallisation. In discotics, however, the crystallisation is not made easier by the absence of the top neighbours. On the contrary, here, there are more degrees of freedom at the surface which encourage disorder in the stacks. Premelting of surfaces of this type is usual for most van der Waals solids.[24] The melting starts at the surface and, in a van der Waals solid, propagates into the bulk with a width $\xi \sim \lambda\{(T_M - T)/T_M\}^{-1/3}$, where T_M is the melting temperature and λ a parameter which depends on the thermodynamics of the two phases.[25] This behaviour is also expected to be true for the surface of a discotic liquid crystal, and this is shown schematically in the lower portion of Fig. 3. When a lateral field is applied to such a film conduction is likely to be dominated by that of the disordered surface since, in the bulk, it would be perpendicular to the columns. We have attempted to study the conductivity of discotic liquid crystal surface films using the interdigitated

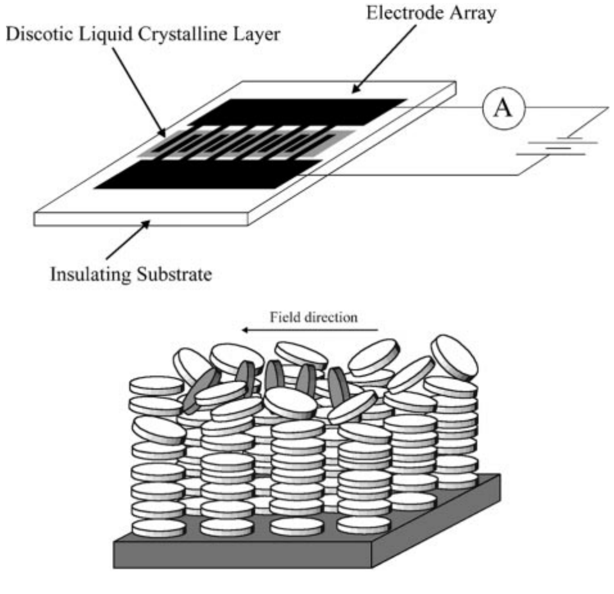

Fig. 3 (Top) The interdigitated electrode geometry used for measuring the free surface conductivity and gas sensing response. (Bottom) Schematic representation of a segment of a homeotropically aligned film with a disordered surface.

electrode geometry shown in the upper part of Fig. 3. The electrode spacing is ~4 μm, and height ~0.2 μm and the gaps between the electrodes are filled with homeotropically aligned discotic liquid crystal. We have measured the conductivity as a function of temperature for a variety of different discotic liquid crystals. The results are shown in Fig. 4 and a scaled version of the same results in Fig. 5. Experimentally, the onset of the temperature dependence of the conduction appears to be related to but is lower than the melting points of the discotic liquid crystals. This is shown in Fig. 6. The onset of the temperature dependent conduction starts well before the actual bulk melting temperature is reached. The conductivity increases with temperature and eventually saturates when the (bulk) material is in the isotropic phase. There are a number of reasons why we think that, in the crystalline and liquid crystalline phase, the film near the surface carries most of the current. We suggest that the initial temperature dependence is probably due to thermally enhanced tunnelling near the surface. Thermal fluctuations in the bulk which could assist the perpendicular carrier diffusion and which could also be the explanation for the initial rise have been shown by Warman *et al.*[26] not to help the perpendicular diffusion rates of electronic charges. In fact Warman has shown that the activation energy for perpendicular electronic diffusion is negative. Clearly the observed behaviour has to do with melting and, in discotics, melting starts at the surface. Consider two models of conduction. In the first model we assume that the temperature dependence is exclusively due to the phase change: the mobility μ changes suddenly with phase, but otherwise remains constant with temperature.[11] If we assume a van der Waals melting law, then in this model, the conductivity should be a sum of the bulk value and the surface film value and obey the relation given by eqn. (2),

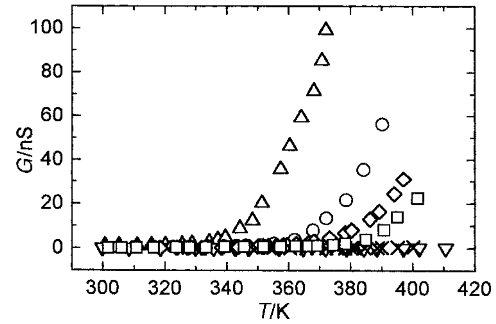

Fig. 4 The conductance G measured using the interdigitated geometry shown in Fig. 3 as a function of temperature T for six different discotic materials. □ = HAT5 (2,3,6,7,10,11-hexapentyloxytriphenylene), ○ = HAT6 (2,3,6,7,10,11-hexahexyloxytriphenylene), ▽ = polymer derivative (reference 35), × = HAT6-NO$_2$ (2,3,6,7,10,11-hexahexyloxy-1-nitrotriphenylene), △ = HAT11 (2,3,6,7,10,11-hexaundecyloxytriphenylene), ◇ = HAT6 with a glass cover. Note that the effect is diminished when a glass cover is added further supporting the view that the observed effects are characteristic of the free surface.

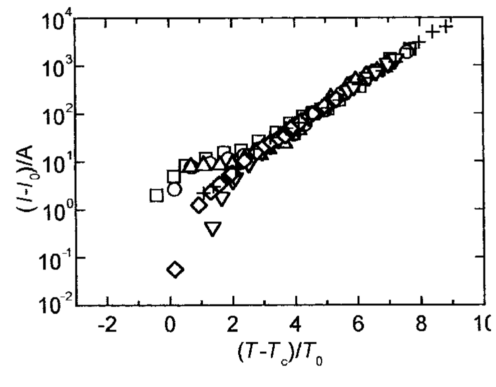

Fig. 5 The data in Fig. 4 re-plotted using the empirical scaling law shown in eqn. (3). □ = HAT5, ○ = HAT6, ▽ = polymer derivative (reference 35), + = HAT6-NO$_2$, △ = HAT11, ◇ = HAT6 with a glass cover.

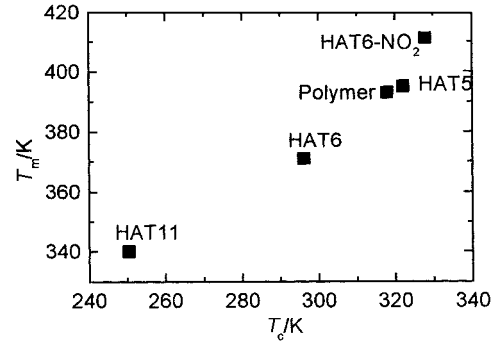

Fig. 6 The critical temperature T_m in the scaling law shown in Fig. 5 and eqn. (3) *versus* the true clearing (melting) temperature T_c of the liquid crystals.

$$\sigma \sim \sigma_b + eN_c\lambda\{T_M - T)/T_M\}^{-1/3}\mu_I \tag{2}$$

where μ_I is the isotropic mobility starting at the surface, λ is a function of the particle number, the free energy and the wetting coefficients of the two phases,[24] T_M is the clearing temperature into the isotropic phase, N_c is the number of electronic charges and σ_b the bulk perpendicular conductivity $[\sigma_b = N_c e \mu_\perp]$ is due to bulk ionic impurities. The data do not fit the simple melting model given by eqn. (2). In fact the conductivity appears to obey universally for all discotic liquid crystalline materials, a 'fluctuation assisted tunnelling conductivity' law of the type shown in eqn. (3).

$$\sigma = \sigma_0 + \sigma_1 \exp\left[(T - T_c)/T_0\right] \tag{3}$$

Here T_c is a material parameter proportional to the melting temperature[27] and T_0 is constant. This Debye–Waller fluctuation type law (3) can be derived by assuming that carriers tunnel from molecular core to core and that the molecular motion modulates the tunnelling distance.[27] The magnitude of the conductivity, the observed smooth temperature behaviour and the Debye–Waller type law are manifestations of the facts that in the intermediate crossover region between the liquid crystalline and isotropic phase disorder is already present, that the disorder starts at the surface, and that the dynamics in the disordered layer determine the observed temperature dependence, *i.e.* that the latter is due to the transport step (the temperature dependence of the mobility).

V Can one sense gases with liquid crystal surfaces?

If the fluctuation behaviour and thermodynamics of liquid crystal surfaces are influenced by exposure to gases the response could be simply and cheaply measured by looking at the conductance change giving a simple gas sensor. Structural changes do not require strong electronic coupling or charge transfer reactions to surface states, so a sensor built on these principles could also work for detecting weakly interacting nonpolar gases. The adsorbate produces a change in the order, or a change in a structural switching field, and this in turn changes the conductivity or the polarisation response. This is relatively easy to measure. Furthermore, self-organised molecular dynamics prefer to keep charged and uncharged impurities near the free surface of the liquid crystal. The motion of molecules tends, so to speak, to expel the disorder into the surface region where there is space for unwanted configurations.

Fig. 7 shows that, as expected, the conductivity of the free surfaces is responsive to gases. The next question is how to make a selective gas sensor. For this there are two powerful strategies.

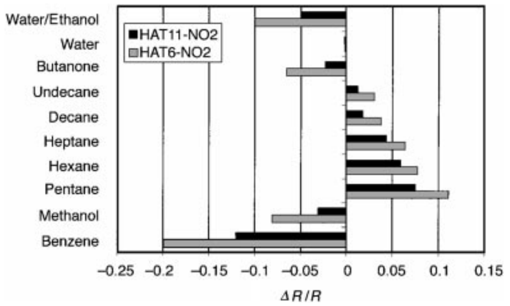

Fig. 7 The gas sensing response for HAT6-NO_2 and HAT11-NO_2 (fractional change in resistance) using the interdigitated electrode geometry.

Firstly, there is the electronic nose principle. This uses an array of sensors based on different liquid crystals and extracts the information by comparing the response vector to known and stored 'smell vectors'. It evaluates the overlap with the 'smell eigenstates'.

The second method is to use the dynamics of the system.[27] In the time domain method, one approach is to pulse the system using a large voltage pulse of say 5 V over 5 μm gaps for 10^{-4} s. This is enough to put charge carriers into conducting bands. One then monitors the time relaxation of the induced polarisation or current. One can monitor the shape of the decays of the measured voltage envelope[28] or the 'noise' on the relaxation function. If the 'noise' contains coherent information (deterministic relations between time values) then these coherent processes show up as resonances in Fourier space. One can then look at the change in the coherent response when the system is exposed to an external perturbation and monitor the nature of this response. In this case the perturbation is a gas, the different components of this gas could in principle each generate its own specific change in the non-random part of the time response. The change can then be picked up by 'listening to the music' in Fourier space. However, there is no guarantee that all components show their presence in the same way, or that some even appear at all, so a working practical device which uses this principle might require considerable development and software engineering. A similar effect can be achieved, though in a different physical context, by subjecting the film to a pulse of light or continuously irradiating it with light. Here the emitted sound can in principle be used to identify the vibrational spectrum of the 'contaminated' film. This technique is known as Photo Acoustic Spectroscopy and has been used with success in liquid crystals to measure their thermal properties.[29] We have shown that the 'coherent noise' principle seems to work well with the voltage pulse as the exciting pulse and the Fourier analyser as the receiver.[27] The method works with precision and apparently gives an almost one-to-one correspondence between the components in the gas mixture and the coherent signals in Fourier space, when one uses discotic liquid crystals or conjugated polymers as the sensitive layer.[30]

When translated into the language of classical physics, quantum coherence implies the presence of deterministic processes and therefore the presence of forces. As mentioned above, we believe that it is the Coulomb forces which indirectly cause the resonances in the relaxation response of the voltage pulsed gas sensor.[31] The effect will probably occur in any other dielectric in which small perturbations in electronic properties or structure cause large changes in the time response of the trapped or stored charge *i.e.* in systems in which weakly screened charges move in low dimensional pathways and in which space charge barriers can be self-created and self-destroyed. This should include the majority of conjugated polymers, columnar liquid crystals, nano-engineered ultra fine wires,[32] hybrid surfaces with ultra thin channels, nanotubes[33] and nanoparticle assemblies.

VI Conclusions

For opto-electronic applications, and in bulk form, molecular condensates are usually difficult to exploit commercially because they almost always have electronic energy bands which are too narrow, band gaps which are too large and often they are too unstable.

However, one of the most promising applications of discotic liquid crystals is in the field of environmental sensing where one exploits the rich variety of structural organisations and the ease with which one structure can change into another. Liquid crystal gas sensors are cheap and give a sensitive response. Oxygen stability, water insensitivity and self-repairing surface dynamics give some liquid crystals and particularly charge-transporting triphenylenes valuable advantages.[34] Use of antiferroelectric discotics could provide a significant additional advantage, given that the other technical requirements are also satisfied. In antiferroelectrics, disorder and fluctuations work together to generate net dipole fields, and these are easily detected as changes in capacitance. Selectivity can be achieved by using 'nose arrays' and time nose array processing or by working in the linear or nonlinear coherent time response domain.

Despite some remarkable recent successes in understanding and harnessing the properties of discotic liquid crystals, there are still a large number of unknowns. For example we still know very little about the free surface, the molecular dynamical details of how the surface organises itself as a function of temperature, and how it responds to various types of adsorbates. This applies particularly to dipole carrying materials. We also still need to know much more about the nature of the coupling of discotic liquid crystals to surface states, their alignment and limits of their chemical stability. Exploiting the full technological potential of these materials needs answers to these questions and there is still a considerable amount of theoretical and experimental work to be done.

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