

Discotic liquid crystals – Self-organizing molecular wires*

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WHEN considering the possibility of commercially viable applications for discotic liquid crystals, it is worth noting that in the case of calamitic liquid crystals some 80 to 90 years elapsed between their discovery in 1888 and their first application in displays. Since discotic mesophases were only discovered in 1977 (ref. 1), it is not surprising that the first applications are yet to be realized.

Recent research has established that the individual molecular columns in discotic liquid crystals can act as molecular wires for the transport of charge^{2,3} or excitons^{4,5}. This unique property is set to give rise to commercial applications in fast high-resolution light scanning and xerography, and in environmental gas sensors in the immediate future, and, in the longer term, to hybrid computer chips which will enable us to communicate electronically with molecules.

The reasoning behind this optimistic vision of the prospects for discotics is discussed in the context of recent and current research.

Discotics as arrays of molecular wires

The high mobility of charge carriers along the individual molecular columns (wires) in discotic liquid crystals stems from their unique architecture. They are comprised of disordered stacks of disc-shaped molecules, such as the hexaalkoxytriphenylenes, arranged on a two-dimensional lattice (Figure 1). The separation between the aromatic cores is of the order of 3.5 Å, so that considerable overlap of π^* orbitals of adjacent aromatic rings occurs. This produces a quantum band structure along the columns with a band gap of 2–4 eV and a band width of approximately 0.1 eV. Charge carrier mobilities are in the range 10^{-2} to 10^{-5} cm² V⁻¹ s⁻¹ and typically at least 10^3 greater than the corresponding mobilities in the perpendicular direction. The perpendicular transport is fluctuation controlled or impurity assisted.

Long-range one-dimensional transport is generally not realistic in molecular solids due to the presence of structural defects, or deep traps. However, in discotic mesophases the liquid-like fluctuations in columnar or-

der, which take place on a time scale of less than 10^{-5} s, provide a 'self-repairing' mechanism.

This combination of properties is quite unique and opens up new opportunities for applications of liquid crystals.

Applications

Fast, high-resolution xerography

Recently it has been demonstrated that mobilities for photoinduced charge carriers in the columnar phases of pure, triphenylene-based discotic liquid crystals are of the order of 10^{-4} to 10^{-3} cm² V⁻¹ s⁻¹ (refs 3, 6) and are as high as 0.1 cm² V⁻¹ s⁻¹ in the highly-ordered helical phase of hexahexylthiotriphenylene⁷. This makes them suitable for use as the active charge transport layer in fast and high resolution xerographic and laser printing applications.

For the last 30 years, polymer organic photoconductors have been widely used as photoconductive media in the field of xerography and laser printing. The efficiency of photocopiers and laser printers is primarily due to the mobility of charge carriers in the photoconductive layer. Polyvinylcarbazole (PVK), for instance, exhibits a mobility in the range of 10^{-6} cm² V⁻¹ s⁻¹. However, this is too slow for application in fast laser printing and photocopying, and toxic inorganic compounds of selenium and tellurium are therefore used.

The surface field effect gas-sensor

The present generation of 'electronic noses' are based on an array of 16–32 individual gas sensors, each made from a conducting organic polymer which displays reversible changes in conductivity when exposed to polar volatile odours. Although the response is non-specific to individual odour molecules, a characteristic odour 'fingerprint' is obtained from the response of an array of sensors. However, a serious limitation of conducting polymers is the lack of response to non-polar molecules.

The surface of a discotic liquid crystal has a unique topology (Figure 2). Fluctuations in the lengths of the columns result in a 'conductive' surface layer. The

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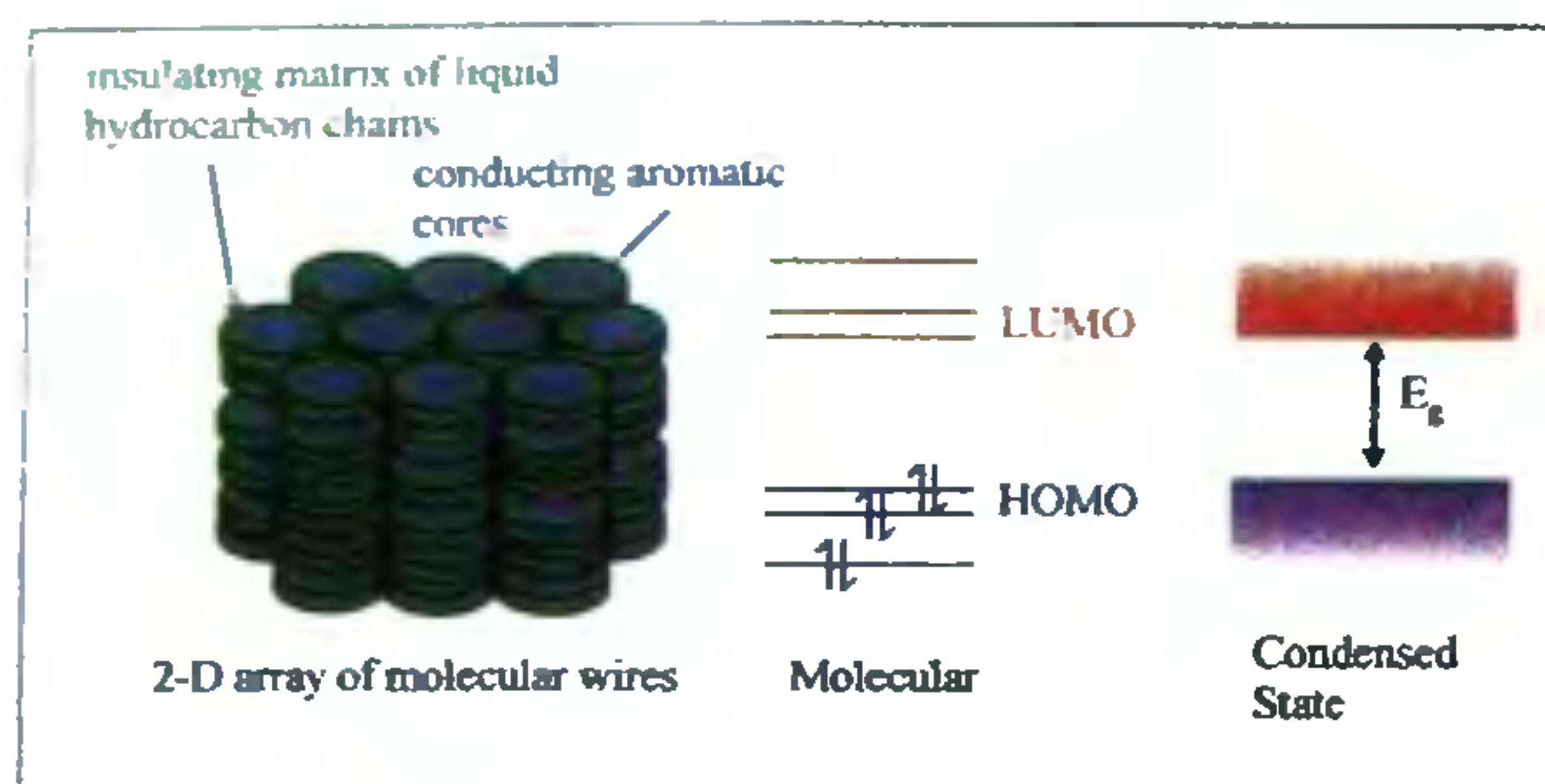


Figure 1. A schematic view of both the D_h phase in discotic liquid crystals and a simplified electronic structure of an isolated molecule and the condensed state showing the band gap E_g .

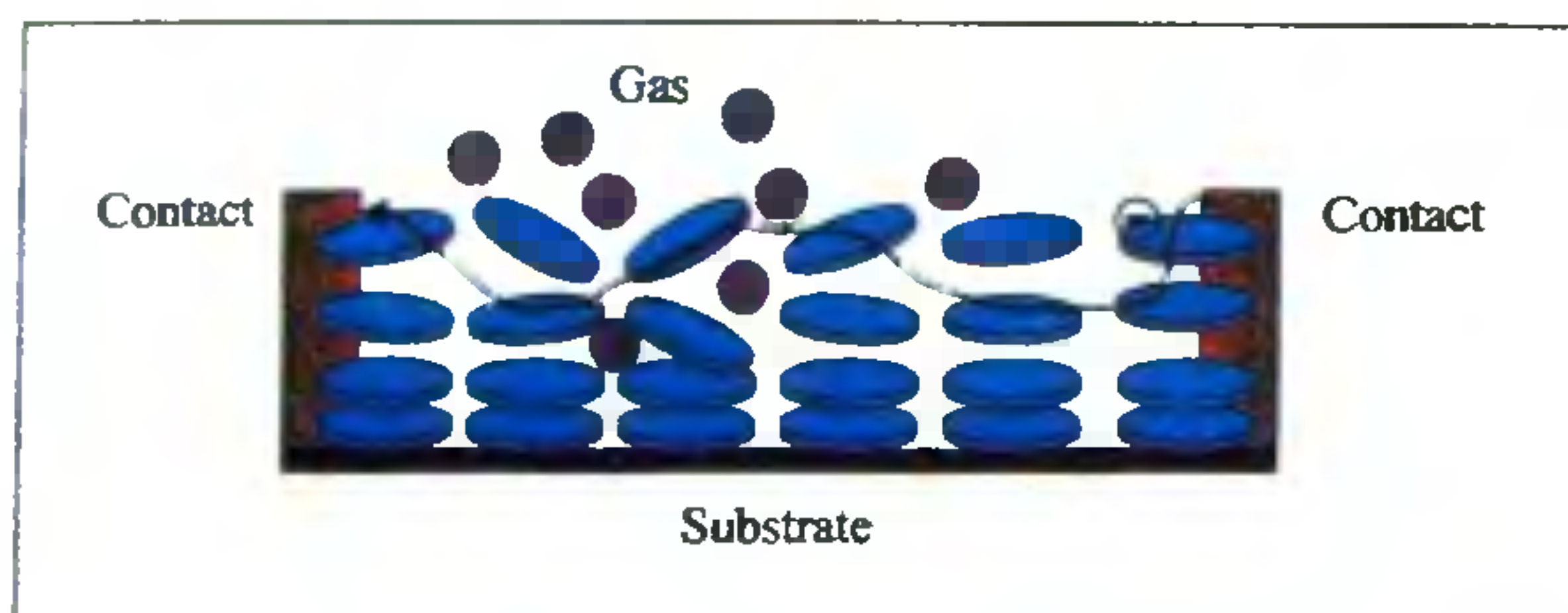


Figure 2. A schematic illustration of a gas sensor exploiting the surface conductivity of the discotic liquid crystalline film.

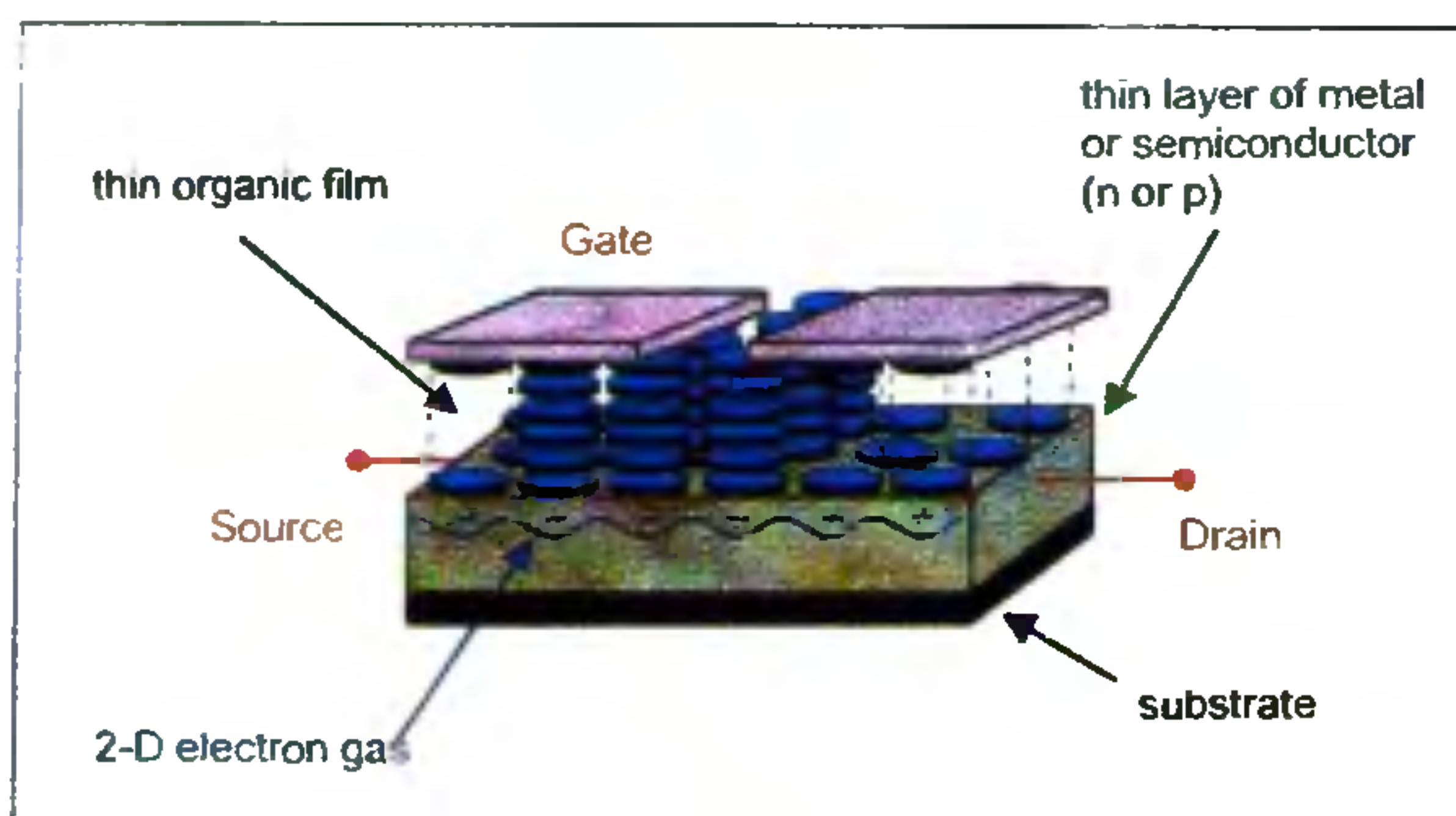
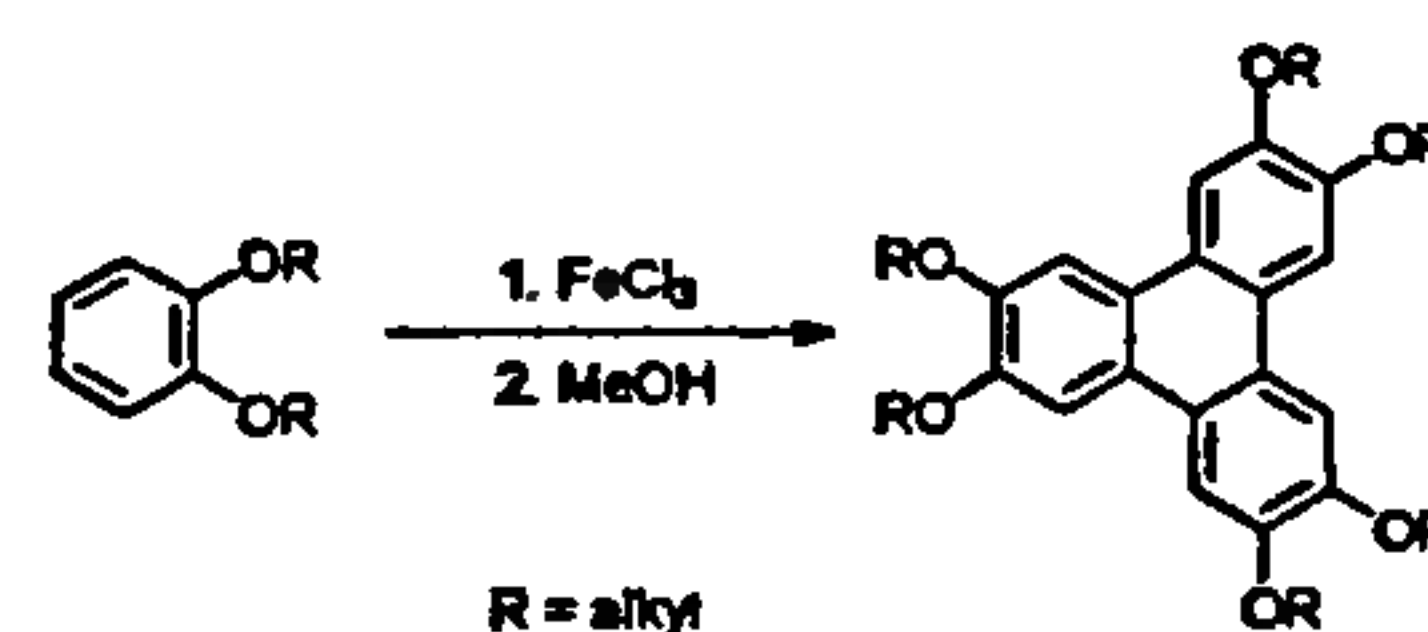
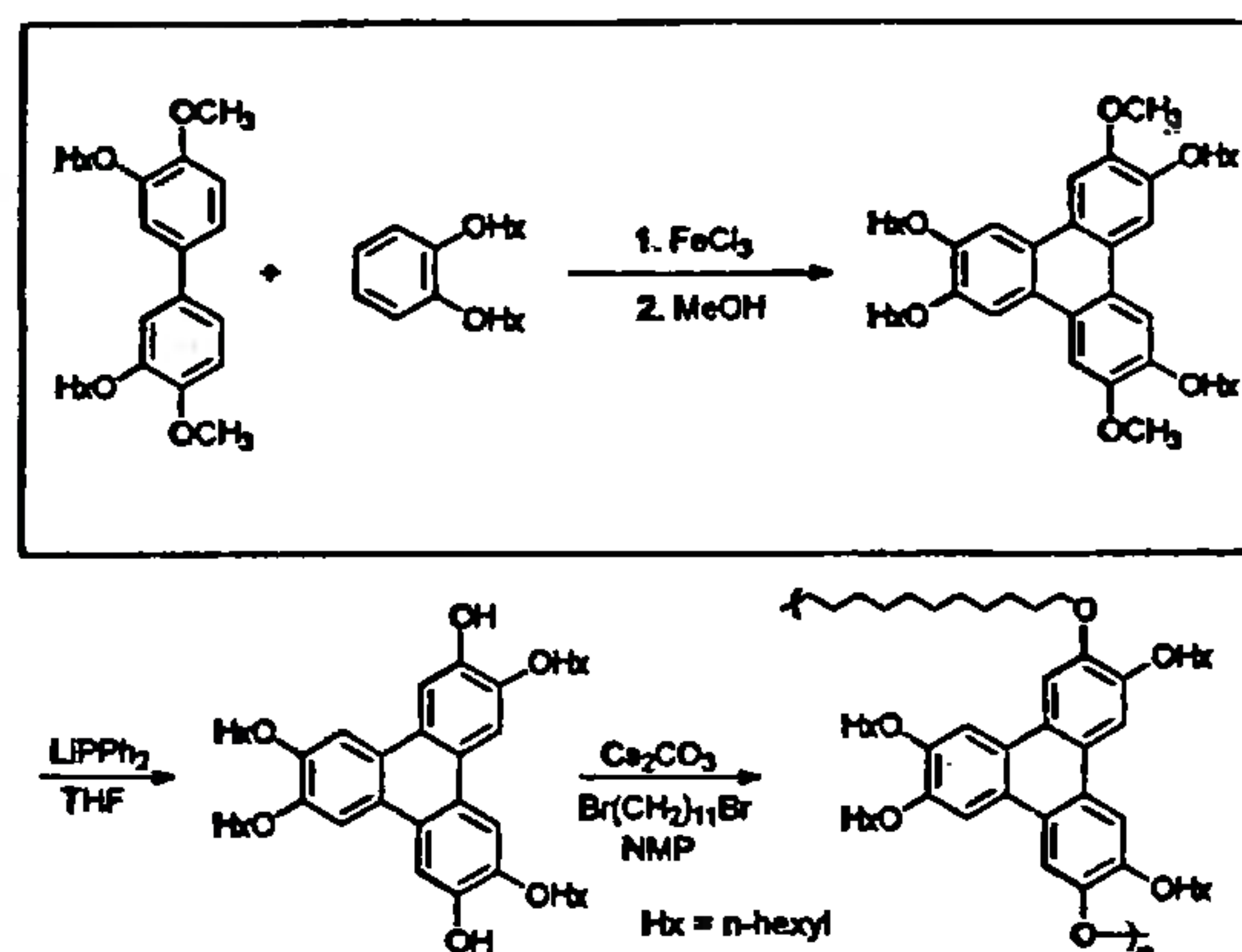


Figure 3. A schematic view of a hybrid discotic liquid crystal/silicon field effect transistor. The molecular wires generate a 2-D band structure in the silicon inversion layer. The source-drain current is therefore sensitive to signals along the columns produced by sensing molecules absorbed in the film.

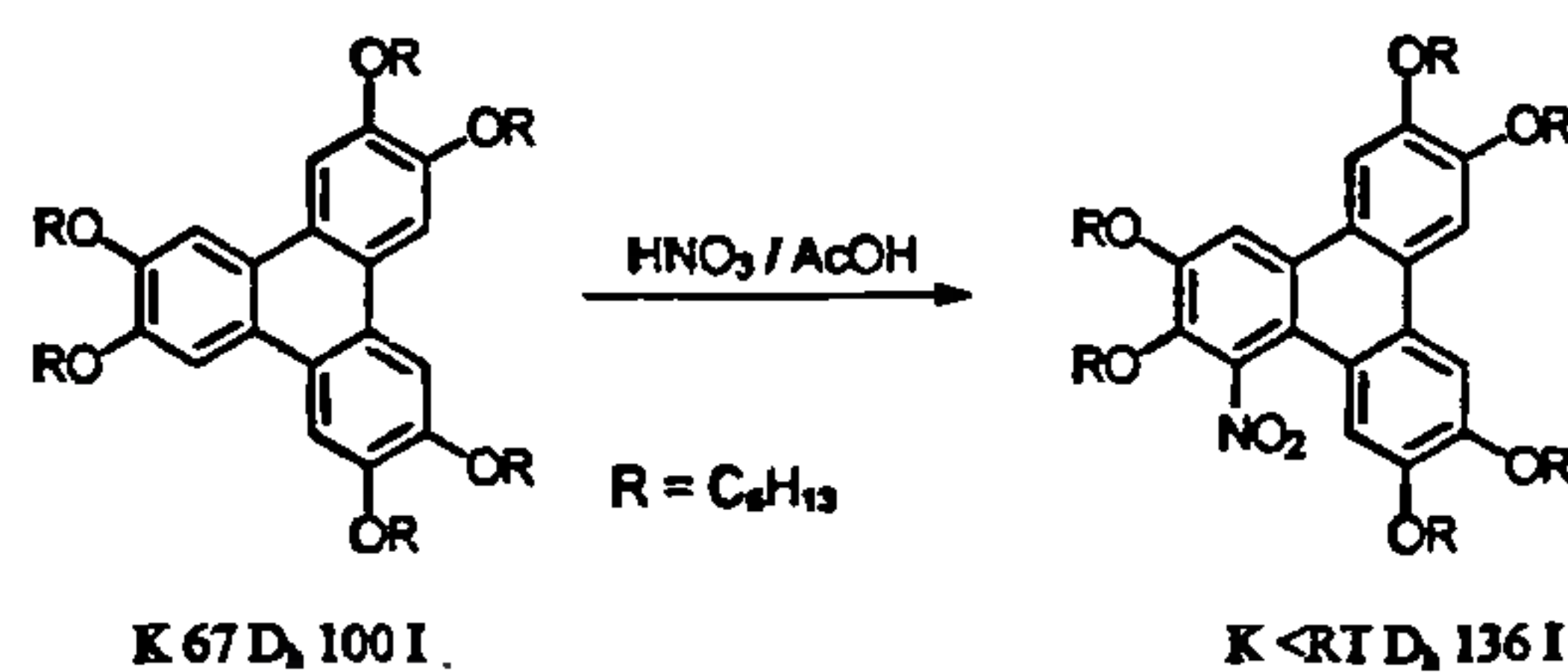
carrier mobility along the surface is fluctuation assisted and the tunnelling rates are exponentially dependent on the molecular core spacings. The core-core separation fluctuates with the surface and changes as soon as the surface is disturbed: i.e. locally melts, freezes, reorients, etc. The electrical conductivity of this surface layer is, therefore, very sensitive to the absorption of molecules. Discotic liquid crystals can therefore be used



Scheme 1. Synthesis of 2,3,6,7,10,11-hexaalkoxytriphenylenes.



Scheme 2. Synthesis of unsymmetrical triphenylene polymer precursor.



Scheme 3. Nitration of 2,3,6,7,10,11-hexahexyloxytriphenylene

as very sensitive gas sensors for both polar and non-polar molecules. The response has a physical origin and does not rely necessarily on charge transfer between the adsorbed molecule and the discotic aromatic core.

Communicating with molecules

The narrow electronic band structure, and the slow speed of response in discotic liquid crystals rule out many traditional semiconductor applications. We can, however, envisage applications for hybrid systems which combine the unique electronic properties of discotic liquid crystals with current silicon technology (Figure 3). Discotic liquid crystals form high-quality insulating films and could, therefore, replace the traditional oxide insulating gate in a field effect transistor. The novel feature now is that self-assembled molecular

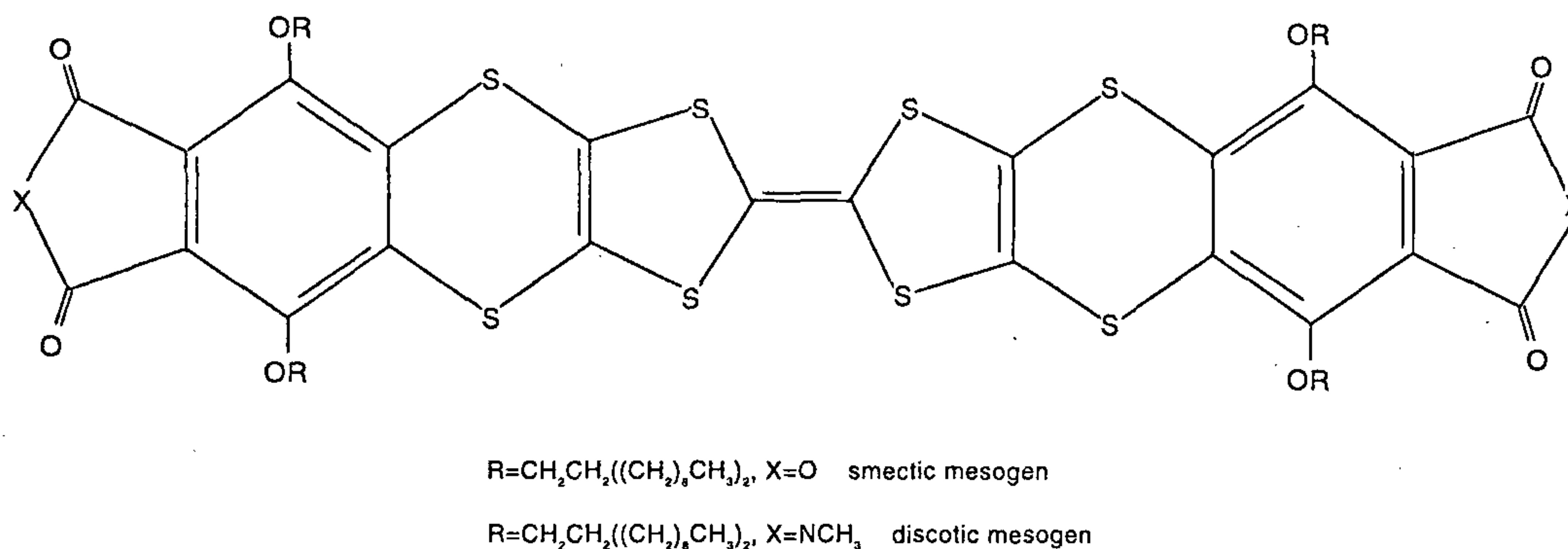


Figure 4. Examples of smectic and discotic tetrafulvalene mesogens.

wires in the liquid crystal can address the 2-D electron gas in the inversion layer of the silicon. This coupling is strong enough to give rise to a hybrid band structure in the inversion layer with the effect of amplifying perturbations in the molecular wires via restrictions imposed on quantum pathways. In this way we can transform molecular signals arriving in the molecular wires into electronic signals in silicon chips. Once in the chip, molecular signals, in the form of local current changes, or channel switching events ('on-off'), can be processed in the usual way.

Developments in design and synthesis

In our work we have used mainly hexaalkoxytriphenylenes. They are stable to heat, light and redox processes and their chemistry is fairly accessible. We are now able to produce large quantities of these materials of high purity and at an economic price. Routes for synthesizing low molar mass discotics⁸ (Scheme 1), polymeric discotics⁹ (Scheme 2), and for introducing substituents into the triphenylene ring¹⁰ (Scheme 3), are now available. The latter enables the electrical properties and phase behaviour to be fine-tuned. Device applications of discotic liquid crystals require the development of materials which are liquid crystalline at room temperature and can be easily processed as polymers.

Smaller band gaps can be achieved by using porphyrin, phthalocyanine or larger delocalized aromatic cores. Tetrathiafulvalene (TTF) and its many derivatives are principally studied in the context of solid state organic metals and superconductors. Significantly, we have recently made derivatives of (TTF) which, depending on

minor modifications to the core structure shown in Figure 4, form either smectic A or columnar discotic phases. In the former phase type there is no evidence of π - π stacking between the TTF cores and hence no pronounced electronic band structure in the material. The discotic phase, however, possesses ordered columns of TTF molecules arranged on rectangular lattice. We are currently investigating the electrical properties of this remarkable material. Thus by intelligent design, it is possible to introduce exciting functionality into discotic phases with the prospect of new applications for liquid crystals.

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