

Dr Richard J. Bushby**Recipient of the RSC Josef Löschmidt prize***Career**

Imperial College, London (*B.Sc.* 1965).
 Balliol College, Oxford (*D.Phil.* 1968) Postgraduate student-ship with Professor Sir Ewart Jones and Dr G. H. Whitham.
 QMC, London (1968–1969) Postdoctoral Research Assistant with Professor B. C. L. Weedon, Professor J. H. P. Utley and Dr K. Sales.
 Yale University (1969–1970) NATO Fellowship with Professor J. A. Berson.
 University of Leeds (Since 1970) currently Reader in Organic Chemistry and Deputy Director of the SOMS (Self-Organising Molecular Systems) Centre.

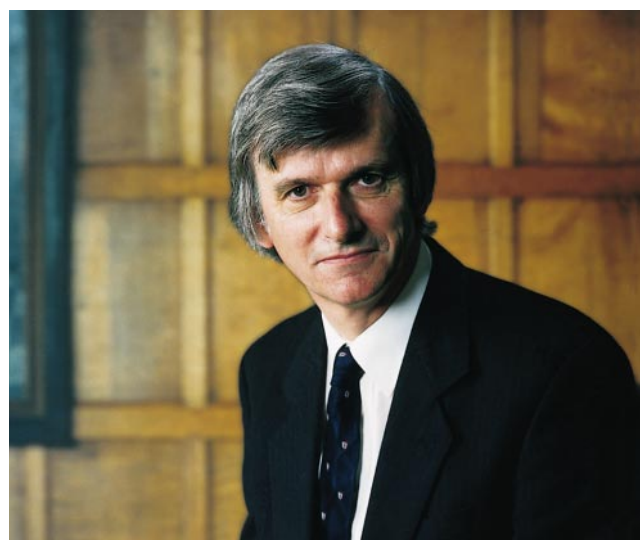
Research

Perhaps the most exciting new frontier for Physical Organic Chemists is that developing at the interface between Organic Chemistry, Materials Science and Solid State Physics. The challenge here is to create novel molecular materials and to understand and exploit their bulk properties. Hence, in recent years, the emphasis of my own research has shifted from traditional Physical Organic Chemistry (carbanions,¹ ion pairs,² biradicals,^{3–5} MO, LFER¹ and FF² methods) towards 'materials science' and my current work is almost wholly concerned with three topics; molecular magnets, discotic liquid crystals, and substrate-bound biomembranes.

Molecular magnets

Our ultimate aim is to produce conjugated polymers which exhibit ferromagnetism.⁶ Conventional magnetic materials based on transition metals and metal oxides are generally electronically conducting, optically opaque, dense, insoluble, high melting and need to be processed at high temperatures. Organic materials are mostly insulating, transparent, light materials that

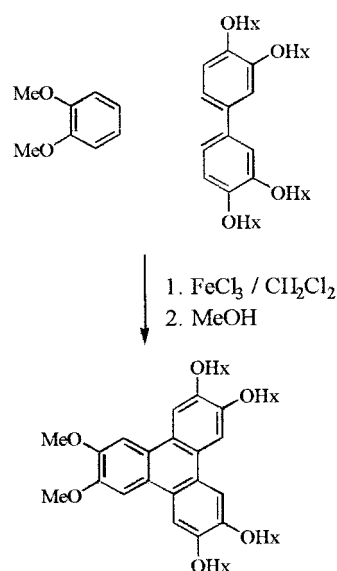
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are soluble and easy to process at low temperatures. Hence a magnetic organic polymer is a highly attractive prospect and, in principle, the design of such polymers is simple. In practice progress has been slow and, despite claims to the contrary, no authentic magnetic organic polymers exist. Our approach is based on doped polyarylamines in which triarylammonium ions (Ar_3N^+) are the stable $S = 1/2$ 'spin-bearing unit', and *m*-quinodimethane is the 'ferromagnetic coupling unit'.^{7,8} Recently we have shown that we can create clusters of up to 30/40 ferromagnetically coupled spins.⁸ This is a significant improvement on the situation of a couple of years ago. It should be possible to improve on this and (hopefully) produce materials with useful bulk properties.

Discotic liquid crystals

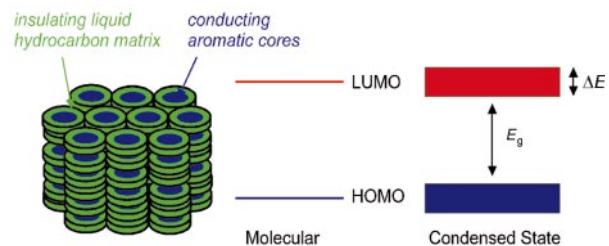
Progress towards applications of discotic liquid crystals was significantly impeded by the difficulty of obtaining sufficient quantities of pure materials. Hence a major part of our effort has been directed towards developing routes that allow them to be made pure, simply and on a useful scale.^{9–11} Among the reactions we have developed, variants on that shown in Scheme 1



Scheme 1 An example of the ferric chloride oxidation–methanol reduction protocol used in the synthesis of triphenylene-based discogens.¹⁰

have proved particularly fruitful. It is a reaction which appears straightforward until one enquires why only cross-coupling and no self-coupling products are observed!

It seems probable that applications of discotic liquid crystals will stem from their unique supramolecular architecture and be based on some combination of their alignment and conduction properties. Within the columnar phases of discotic liquid crystals the aromatic nuclei stack into columns (Scheme 2). These are ordered on a two-dimensional lattice, the space between the columns is filled with molten alkyl chains. Surface forces (normally) orient thin films in a homeotropic manner (such that these columns rise perpendicular to the surface). Most have a low intrinsic charge-carrier concentrations but charge carriers can be injected into these columns either chemically,¹² from an



$$\sigma = ne\mu$$

	$\sigma/\Omega^{-1}\text{cm}^{-1}$	$\mu/\text{cm}^2\text{V}^{-1}\text{s}^{-1}$	n/cm^{-3}	E_g/eV	$\Delta E/\text{eV}$
HATn	10^{-13}	4×10^{-4}	10^{10}	4	0.2
TTF-TCNQ	500	1	10^{21}	2	0.2–0.5
Si	10^{-3}	10^2	10^{13}	1.1	3–4

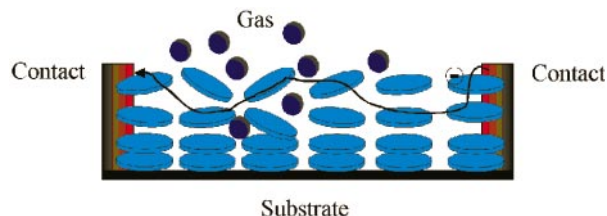
Scheme 2 ‘Molecular wire’ like structure of the columnar phase of a discotic liquid crystal and a comparison of the significant properties of hexaalkoxytriphenylene discotics (HATn) with those of the organic conductor TTF-TCNQ and with silicon.

electrode surface¹³ or photochemically.¹⁴ The columns then act like ‘molecular wires’ with the charge carriers hopping along the columns from aryl ring to aryl ring¹⁴ while the surrounding sheath of molten alkyl chains partly ‘insulates’ each column from its neighbours. Because of the fluid, disordered nature of the columns charge carrier mobilities are lower than in crystalline organics but this disadvantage is more than offset by the fact that these systems ‘wet’ electrode surfaces, can be aligned on a bulk scale and imperfections are rapidly healed away.

One area of application of conducting discotic liquid crystals we are investigating is as gas sensors (Scheme 3). Conduction through the air/liquid crystal interface proves particularly sensitive to perturbations caused by dissolution of small amounts of gaseous materials.¹⁵

Substrate-bound biomembranes

In detecting and identifying low concentrations of biomaterials we need to find ways to exploit nature’s own systems. We cannot hope in our molecular designs to surpass what nature has perfected over millions of years of evolution. Many of nature’s sensors reside in the plasma membrane. Hence the attraction of trying to ‘pin’ biomembranes to electrodes and other sensitive surfaces and in trying to create artificial cell elements. Our most successful systems to date¹⁶ use micro-contact printed self-assembled monolayers based on a cholesterol derivative.¹⁷ These generate micron-sized wells capped by bilayer mem-

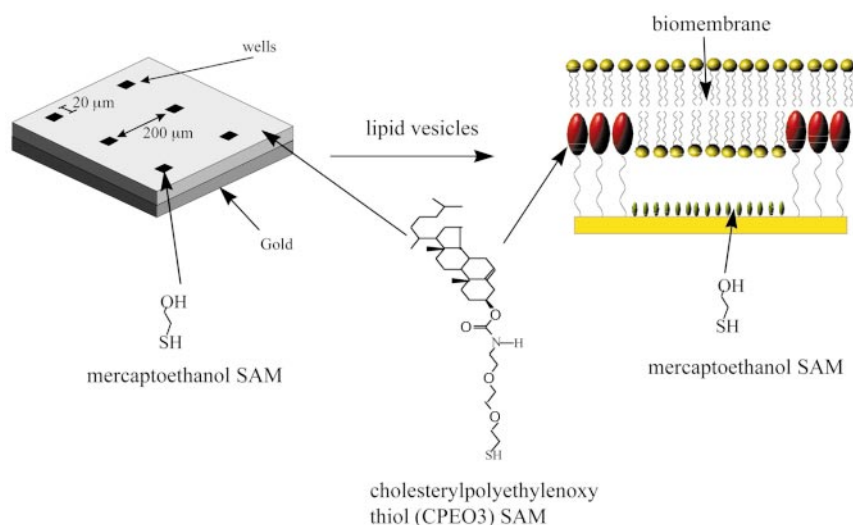


Scheme 3 Schematic representation of conduction through the surface film of a homeotropic film of a discotic liquid crystal.

branes (Scheme 4). These are capable of supporting the activity of very simple ion-transporting solutes such as gramicidin and valinomycin.¹⁶ The development of more advanced systems is in progress.

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Scheme 4 Schematic representation of the formation of tethered biomembranes on stamped self-assembled monolayers.