GEORGE WILLIAM GRAY CBE MRIA FRSE
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Elected FRS 1983

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George Gray was a renowned British materials chemist, internationally distinguished for his research into liquid crystals and their applications in flat-panel displays. His seminal invention of the liquid-crystalline cyanobiphenyls underpinned the creation of the modern electronic displays industry, which began with digital watches and has continued through to smart and three-dimensional televisions. There are now more liquid crystal displays in the world than people, and these devices have engendered societal changes through social networking on the Internet. His ability to design, synthesize and utilize self-organizing materials across the various disciplines of science showed that he was a supreme molecular engineer. For his contributions to soft-matter and related advanced technologies he was made a Commander of the British Empire, Kyoto Prize laureate, Fellow of the Royal Society, Fellow of the Royal Society of Edinburgh and Honorary Member of the Royal Irish Academy.

EARLY YEARS AND FAMILY

George Gray was born to John and Jessie Gray in Denny, Scotland, on 4 September 1926. He was an ordinary, happy and mischievous boy brought up in a stable and loving family. He was the only son, but he did have a sister, Catherine, six years his senior. As a child his main interests were making models of ships, reading, and growing plants and gardening. The small town of Denny, where he grew up, was not particularly attractive because it was centred on coal mining, paper manufacture and iron production. However, as it had easy access to the surrounding and beautiful countryside, his memories were of hills and rivers, not industrial grime.

George’s mother was much closer to his sister than she was to George; maybe she found him too lively, untidy and mischievous—for example, he once tied his nanny to a chair. In

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later life they came to understand one another much better. His father, on the other hand, was a great friend to him. He was the pharmacist in Denny, and a trained chemist and botanist, to whom George owed his early interest in science. George’s father ran his own business, and it was through being allowed to help in weighing materials and making pills, powders and solutions that George developed a special interest in chemistry. His father used to take George on walks on Sundays, and would talk to him about plants, their medical components, and the chemistry of living processes. Thus, by the time he was 10 years old, George was conversant with atoms and molecules that constituted living and materials systems, and from that point he never wanted to be anything other than a chemist.

His father influenced him strongly along the way as George’s interests in science developed. He possessed a collection of books on the history of science, from which George learned about the achievements of scientists such as Faraday, Black, Priestley, Gay-Lussac and Lavoisier. This made him keen to achieve in science, an attitude that was strengthened when he went to the University of Glasgow and was actually taught by leading research chemists such as J. W. (later Sir James) Cook FRS, the eminent steroid chemist, and J. Monteath Robertson (FRS 1945), at that time the youngest UK university professor and a famous X-ray crystallographer. In addition to studying chemistry during the war years, George also took subsidiary subjects in mathematics and physics, graduating in 1946.

Two issues then were implicated in George’s move south of the border to the remote and war-torn city of Kingston upon Hull. First, George’s father became seriously ill and could not afford to support him through a research degree. Second, George met Professor Monteath Robertson in a corridor in the department at Glasgow. Monteath informed George that there was a temporary post as a laboratory demonstrator at the University College of London (Hull), and that his friend Brynmor Jones was moving there from Sheffield University to become Professor of Chemistry. At that time there was only one post of professor in Hull, but as the college progressed towards receiving its Charter, Brynmor moved upwards to become its Vice Chancellor and was later knighted by the Queen. At the time George had also been offered employment with the Anglo-Iranian Company in Persia, but he turned this down for the opportunity to work in the Department of Chemistry at Hull, where he stayed for the next 40 years. George must have been successful in his first year at Hull because he was quickly appointed as an assistant lecturer. Professor Brynmor Jones pointed out that as a full member of staff he could now study for a higher degree, and suggested two topics, one in reaction kinetics and the other in liquid crystals, which Brynmor had made initial studies on (Jones 1935). George chose the riskier topic of liquid crystals and subsequently submitted his thesis in 1953 entitled ‘A study of the synthesis and mesomorphism of certain aromatic carboxylic acids’ for the degree of Doctor of Philosophy in the Faculty of Science of the University of London. After a number of years patiently investigating liquid crystals and cell membranes and teaching organic chemistry, George’s commitment to the university was recognized by his promotion to the position of Senior Lecturer in 1960. His successes and growing reputation saw him promoted to Reader in Chemistry in 1964, and at the age of 52 years to Professor of Chemistry in 1978. Later he went on to become the Grant Professor of Chemistry and Head of Department. Reflecting on his time at Hull, Gray commented (24)*:

> It was a challenging environment in which to work, perhaps more so than in some better heeled institutions—everyone was keen to succeed, to help one another, and to recover after the lost war-

* Numbers in this form refer to the bibliography at the end of the text.
time years. Indeed I owe a great debt to the University of Hull, giving me as it did freedom to do research, develop my own ideas, gain promotion and work in a steadily improving environment supported by many excellent colleagues. Because of this, I remained at Hull for over 40 years before leaving in 1990, after serving as Head of Chemistry and senior Professor.

When George moved to Hull he also met Marjorie Canavan, who worked in pharmacy and nursing. They married in 1953, and subsequently had three daughters. The eldest, Veronica, has three children of her own; Elizabeth was their second daughter, who passed away a few years before George and Marjorie; and the youngest, Caroline, has a son. Possibly following in her father’s footsteps, Caroline became an organic research chemist with the pharmaceutical company SmithKline Beecham, working on the synthesis of new pharmaceutical products. Marjorie and George were a loving and endearing couple, and there was always a warm and fun-loving glow around them. Talking about Marjorie, George said ‘a scientist (like me) who gives a lot to science sacrifices a lot of his life and time to that process, and he needs behind him a very good woman. I was lucky to have that in my wife’ (24). Thus, it was touching that they passed away within two weeks of one another.

The University of Hull, 1946–70

To place George Gray’s life of research in organic materials into context, it is worthwhile considering the nature and practical uses of liquid crystals. At the time that George began his research in Hull, liquid crystals were being investigated by only a few scientists across the world; maybe 100 at most. However, by the turn of the millennium liquid crystals used in flat displays had become ubiquitous, with more liquid crystal devices in the world than people. Moreover, their uses in communication devices have resulted in massive societal changes. Apart from displays, liquid crystals have found applications in high-yield-strength polymers (for example Kevlar), low-viscosity fluids (to lubricate computer disc drives), thermochromics (strip thermometers) and gels (for example Cif), to name but a few. They have become the quintessential organic materials of the modern era, and are thought of by many as a fourth state of matter, bridging solids and liquids. Their unique properties are based on the anisotropic shapes of their molecules, which are either rod-like (prolate) or disc-like (oblate), and on their abilities to self-organize into fluid-like phases. The fluidity of their structures permits ease of molecular reorientation by applied external stimuli, such as mechanical, magnetic and/or electrical fields (for an introduction to liquid crystals see Collings (1990) and Collings & Hird (1997)).

With the encouragement of Brynmor Jones, who had already been working on liquid crystals, Gray’s methodical research into the synthesis and characterization of mesomorphic materials started in 1946. Thus Gray’s early work involved the synthesis and determination of the mesomorphic properties of alkoxybenzoic and alkoxyanthoic acids, and was probably based on the 1942 thesis by Y. M. May entitled ‘Preparation and properties of 4-hydroxy-2-naphthoic acids’; May was a research student of Jones’s at the University of Sheffield. In his studies Gray determined the melting-point and clearing-point transition temperatures of homologous series of substituted acids as a function of terminal alkoxy chain length, and in some cases determined the presence of smectic (lamellar) phases. He was later aided in this work by his research student F. Marson, who graduated with a Master’s degree in 1955 with a thesis called ‘Synthesis and mesomorphism of certain substituted n-alkoxy aromatic...
carboxylic acids’. Two observations can be made: first, with the synthesis of substituted biphenyl carboxylic acids it was clear that Gray was already investigating the liquid crystal properties of biphenyls 20 years before he employed the same motif in the structures of the groundbreaking nematogens used in displays, and second, the enigmatic rod-like 3’-nitro-4’-n-hexadecyloxybiphenyl and 3’-nitro-4’-n-octadecyloxybiphenyl carboxylic acids were also prepared (for example see figure 1). These two remarkable materials were described by Marson as exhibiting either two or three smectic phases respectively, but today, as a result of the collaborative work with J. W. Goodby (19), A. J. Leadbetter (20) and J. E. Lydon (Lydon 1984, pp. 75–76), they are known to exhibit bicontinuous cubic (gyroid) phases sandwiched between the smectic A or liquid and C phases as a function of temperature. The fundamental underlying importance of this work was that it showed that curvature of the packing of rod-like molecules could affect the induction of mesophase formation in soft matter systems. Similar effects are now found for ‘blue phases’ (3), surfactants, amphiphiles, micelles, DNA complexes and di-block copolymers, among others (Bruce et al. 2006).

The confidence in the transition temperatures of Gray’s early work can be attributed to his design and construction by the technicians in the Department of Chemistry of an electrically controlled hot stage for attachment to his optical microscope, which allowed samples to be viewed while the temperature was being raised (1). A side elevation and plan of the block are shown in figure 2a. The hot stage consisted of two cylindrical pieces of copper about 4.5 inches in diameter and 0.625 inches thick. Both had a centrally drilled hole 0.5 inch in diameter. A slide slot and aperture for insertion of a thermometer were cut out. Below the lower block a coil of nichrome wire 22 feet long was wound on a mica disc, which was insulated with other mica discs from the copper block and brass plate below, as shown in figure 2b. The heating rate was controlled by using a rheostat; the whole apparatus was insulated with asbestos and covered with a brass outer casing. Glass plates, top and bottom, were used to prevent air currents, and melting points between 40 and 300 °C were determined regularly, via standards, with a high degree of accuracy. This instrumentation was ultimately critical to the liquid crystal research of the era because no methods, other than microscopy, were available for quantitative studies. No doubt Gray’s understanding of dislocations and disclinations in defect textures, and his having access to thermal polarized light microscopic analysis, gave him an internationally leading edge in the field.
In about 1952–53 Gray’s research into liquid crystals expanded beyond the study of the effect of aliphatic chain length and lateral substitution on the mesomorphic properties of materials. Instead he switched his work to the investigation of the design and structure of the central aromatic core unit and the linking groups, usually Schiff bases that were attached to it. With MSc students J. B. Hartley (1954) and P. Culling (1956), and doctoral student A. Ibbotson (1957) the steric effects on the mesomorphism of polycyclic compounds were studied. In particular an attempt was made to establish whether the non-sterically affected biphenyl ring system that Gray had previously been investigating was planar, twisted at a fixed angle about the 1:1' bond, or freely rotating about this bond in the mesomorphic states of its derivatives. This was investigated by preparing the comparative 7-n-alkoxyfluoren-2-carboxylic acids and their alkyl esters, the 2-n-alkoxybenzylideneaminofluorenes, the 2:7-di-(p-n-alkoxybenzylideneamino)fluorenes and the analogous fluorenone derivatives. By comparing the mesomorphic properties of these compounds, in which the tricyclic fluorene ring system was planar, with those of the biphenyl analogues, carrying substituents in the 4 or 4:4' positions, indefinite conclusions were reached. However, they suggested that the biphenyl ring system might be planar in the smectic and nematic mesophases.

Further studies on the 4-p-n-alkoxybenzylideneamino-3'-2':2- and 3-chlorobiphenyls were also made. The nematic thermal stabilities of the 2'-chboro and 2-chloro isomers were found to be much lower than those of 3' and 3 isomers. This was explained by interannular twisting of the biphenyl rings from co-planarity by the chlorine atoms in the ortho positions. The isomeric mono-anils bearing bromine and methyl substituents were found to give similar results. By comparing the mesomorphic properties of mono-anils with different substituents in the 2 position they concluded that the nematic thermal stabilities decreased with increasing substituent size, i.e. with increasing interannular angle, and therefore that free rotation could not occur about the 1:1' bond in the nematic state. The outcome was that for the biphenyl the
interannular angle was suggested to be certainly much less than the 45° in solution, and might be as little as 0°, i.e. the angle for biphenyl in the crystal state.

Although these conclusions were speculative, and have not been upheld by later neutron scattering studies on molecular dynamics in liquid crystals, it is clear that Gray was starting to build property–structure correlations about mesophase formation and stability. His cumulative studies formed the basis for his 1962 book *Molecular structure and the properties of liquid crystals* (2). At the time this was the most important chemistry text ever brought out on the subject of liquid crystals, and it gave Gray international repute. However, he also viewed writing the book as particularly important because he could see a possible end to his liquid crystal research as funding became increasingly scarce.

As his early work on liquid crystals began to bear fruit, the direction of the field began to waver as a result of the subject’s becoming labelled as a scientific curiosity. Looking for ways forward, Gray became influenced by the department’s interest in the kinetics of organic chemical reactions, most notably in the area of the nitration of materials possessing aromatic rings, as seen in Marson’s thesis. The research of Culling saw Gray extend his interests, by default, into rod-like systems based on the terphenyl motif. Although nitration and polynitration of unsubstituted \( p \)-terphenyl were the main topics of the work, Culling also included research into 4-cyano-\( p \)-terphenyl. This initial work was followed by more extensive research by D. Lewis, as reported in his doctoral thesis ‘A study of the nitration of \( p \)-terphenyl’. Figure 3 shows the structures of some of the more relevant materials prepared in Hull on the path towards suitable materials for displays, with the nitro-substituted biphenylyl ester prepared by R. C. Wilson (whose 1963 PhD thesis was entitled ‘Transmission of electronic effects in certain biphenyl systems’) coming very close to the successful design used for the groundbreaking 4-n-alkyl 4’-cyanobiphenyls.

With these studies, which were published as a 13-part series of papers on mesomorphism and chemical constitution in *Journal of the Chemical Society*, Gray developed the following property–structure correlations for the molecular design of liquid crystals, which he later applied extensively in his future research on display materials:

- regular trends in liquid crystal transition temperatures within homologous series;
- the dependence of nematic thermal stability on molecular breadth and lateral substituent size;
- the strong influence of steric twisting by a lateral group in depressing mesophase thermal stability;
- the role of aromatic core size and type on phase type and phase stability;
- core shielding effects in diminishing the depressing effects of lateral groups;
- the important nematic terminal group efficiency order;
• the more subtle dependence of smectic thermal stability on a combination of lateral group size and dipole moment.

Gray possessed the relevant knowhow and skills that underpinned the seminal invention of the liquid crystals that formed the basis of the modern flat-panel displays industry. Ten years later, opportunity arrived and the liquid-crystalline terphenyls were united with their biphenyl analogues, and thereby nematic formulations were produced that had wide operating temperatures for displays that could be used by the electronics industry for applications in the desert and the tundra alike.

However, the inventions of new display concepts were not even on the horizon in 1960, and consequently funding for research into liquid crystals was becoming scarce, particularly for universities such as Hull, and so Gray turned to industry, and in particular to Reckitt & Sons Ltd of Hull for help. Over the following decade the company funded research into bacterial and germicidal action against various organisms, and the investigation of the structures and properties of their lipopolysaccharides. Seven PhD theses resulted from these studies, and as a consequence more than 50% of Gray’s research became involved in the investigation of the cell walls of bacterial membranes, which after all are another form of liquid crystals. One of Gray’s students, S. G. Wilkinson (now deceased), later became Professor of Biological Chemistry at the University of Hull, and so began Gray’s dynasty in the Chemistry Department. Wilkinson once remarked that during his PhD research, Gray carried on studying thermotropic liquid crystals by working at the bench, but that he (Wilkinson) never knew what he was doing. This observation was frequently made in the years to come: Gray was careful about what he divulged, even to his own researchers.

A PROGRAMME ON FLAT-PANEL DISPLAYS, 1970–72

As the 1960s progressed it became clear that funding for liquid crystals would not be forthcoming. Gray had applied to the Science Research Council for support, but was told that he should find a synthesis chemist to work with! This was a point of contention he often raised with the councils. So he seemed destined to work on biological membranes for the foreseeable future. Then in the late 1960s the Radio Company of American (RCA) started to take an interest in alternative displays to the cathode ray tube, and in particular displays based on liquid crystals. This work was not unknown to researchers at the Royal Radar Establishment (RRE) at Malvern; Tom Elliott (FRS 1988) had attended a conference at the National Bureau of Standards in Boulder, Colorado, and heard about and saw a demonstration of a liquid crystal display made by RCA (C. T. Elliott, personal communication). He wrote an internal RRE report on what he had seen, which sparked a lot of interest. The story of how RRE and Hull University began to collaborate in the research of liquid crystals is fascinating, and on such small coincidences do such big discoveries, inventions and societal changes turn. The story was delightfully recalled in his own words by Cyril Hilsum FRS, who was at the time a leading physicist at RRE (Hilsum 1984).

It was on this scene that an exotic figure emerged. He was by no means as well known then as he has come to be, and I use ‘exotic’ in the sense that he was foreign to the context of science and a research laboratory, not with the alternative meaning ‘bizarre’. The story really begins with him, and it is strange to think that the UK liquid crystal fraternity will always be indebted to him. He was the Minister of State for Technology, Mr John Stonehouse. In March 1967,
Mr Stonehouse paid his first visit to RRE, and the conversation with the Director, Dr—now Sir—George MacFarlane FRS ranged over many topics. They touched on the financial return from inventions—the world does not change a lot—and MacFarlane pointed out that UK royalties to RCA on the shadow-mask colour TV tube cost more than the development costs of Concorde. This impressive fact, the truth of which I have never been able to establish, remained in the mind of the Minister during his journey back to London, and festered overnight. Early next morning he rang the Director, and said he was convinced that the UK should mount a programme to invent a solid state alternative to the shadow-mask tube! George MacFarlane was certainly taken aback, but he is a resilient character who does not give in easily. He summoned to his office David Parkinson, then Head of the Physics Group, and me. He explained the situation in which he found himself, and asked what the chances were of RRE making a solid state flat panel colour TV. David turned white, and I said, ‘None whatever’. Neither response offered the basis of a constructive reply to the Minister, so we agreed on the conventional Civil Service reaction—we would set up a Working Party to study the topic.

David Parkinson chaired the Working Party, and by October we were able to recommend work on semiconductor lamps, for very simple displays (Parkinson 1967). This was almost a diversion. The real task of the group was very difficult and time-consuming, because we had to assess effects and materials quite unknown to us. Among the topics brought to our notice early in 1968 were liquid crystals. Here I must digress for a moment and explain the Ministry of Defence system for procurement of electronic components for the Armed Services. Since 1938 this has been the responsibility of an organization with the initials CVD. Until 1950 the initials stood for ‘Committee for Valve Development’, but later it became more appropriate to change to ‘Components, Valves and Devices’. CVD operates through a simple structure of committees, manned by Scientific Civil Servants, each committee dealing with one group of components. It is normal for each committee to organize two or three meetings a year with industrial and academic scientists on particular topics of interest. Now we can return to our theme.

By 1968 CVD had passed the responsibility for Displays to me, and I asked Leslie Large, a scientist in CVD, to organize a meeting on Liquid Crystals. It took place on 1 October. There is no written record of this meeting, but it remains fresh in the minds of several of the participants. The high spot was a review by the person then regarded as the UK authority, and at the end of his talk I called for questions. There being none, I attempted to fill an embarrassing gap, and having noticed that the light from the slide projector, reflected from his liquid crystal sample, cast a curiously shaped and patterned curve on the screen, asked him how this happened. He attempted an explanation, realized this was wrong, remembered a reference to the phenomenon in a book he carried, rapidly turned the pages of this book, decided that the reference was in his loose notes, upended these, dropped both the notes and the book, and then knelt on the floor picking up the pieces. The meeting was rapidly escaping from my control when a quiet voice from the back of the room said ‘I wonder if I can help’. I lifted my eyes from the grovelling body of my key speaker and replied ‘I’d be most obliged if you would’, and my rescuer proceeded to give a succinct explanation. That was the first time I met George Gray. The rest of the meeting was distinguished for the lack of useful knowledge demonstrated by most of our community, and at the end, when Les Large asked if we had reached any conclusions. I replied, ‘Yes, we must put the man from Hull on a contract’. This was easily said, but at that time we had no justification for any liquid crystal programme at all. In fact, in August, in response to a query from MOD Patents Branch, I had written (Hilsum 1984), ‘I may say we are not optimistic about liquid crystals. I would be surprised if our Working Party recommends that work should be started’. I was influenced in this by two inputs to the Working Party a month earlier, one writing ‘Ferroelectrics probably offer the best hope of finding large enough electrooptic effects at room temperature’, and another, ‘Liquid crystals may have a minor role for displays in high ambient lighting, but they will make no impact on Black and White or Colour TV’.
To counter this pessimism, there was in late October a positive report of a liquid crystal electrooptic effect, which might have display applications [Heilmeier et al. 1968a, b]. This came from Heilmeier, Zanoni & Barton of RCA, who demonstrated dynamic scattering, albeit at temperatures between 77 °C and 90 °C. They claimed to have a proprietary mixture operating at room temperature, but gave no details. The record, and all memories, go curiously flaccid at this point, and for a year nothing worthy of mention happened in the UK on liquid crystals. The Working Party ground away, by now under my chairmanship, for David Parkinson had been translated to more responsible tasks. In October 1969, one year after the CVD meeting, the first draft of the Working Party Report appeared, proposing to work on eight topics, but excluding liquid crystals.

The final version was issued in December (Hilsum 1969), and it differed from the draft in one crucial and fascinating respect. The relevant extract read, ‘One system is worth immediate attention. This is the display based on liquid crystals’. Such a volte-face is difficult to explain, particularly since no earth-shattering discoveries were revealed to me in the interim.

The draft had recommended a large programme on ferroelectric ceramics, and a small exploratory contract on liquid crystals. However, Hilsum was unhappy with this and replaced everywhere the words ‘ceramic ferroelectrics’ with ‘liquid crystals’ in the final version, and in April 1970 CVD offered Gray a two-year contract to work on ‘Substances exhibiting liquid crystal states at room temperature’ at a maximum expenditure of £2177 per annum.

A SCIENTIFIC REVOLUTION

The work on materials started in Hull in October 1970 with two researchers, John Nash, who was a postdoctoral fellow, and Ken Harrison (see figure 4), who was appointed to the RRE contract even though he was involved in the writing of his thesis, which was entitled ‘The effects of structural changes on the liquid crystalline properties of certain esters’, for which he was awarded a PhD in 1972.

The initial research at Hull was not particularly well focused. Target structures for new liquid crystals were based on materials reported by RCA and IBM. The preferred devices at that time used the dynamic scattering mode, which required materials with negative dielectric anisotropy (−Δε), and so low-melting materials with rod-like structures and lateral dipoles relative to the molecular long axes were sought. However, purities and problems for many families of materials were soon raised; they were often found to exhibit electrolytical instability, ease of oxidation, or degradation on exposure to ultraviolet radiation. Thus, the Hull group worked on a variety of Schiff bases, azobenzenes, stilbenes, carbonates, carboxylic esters and ultra-pure Schiff bases, among others, but to little effect. However, in 1970 a paper (Leslie 1970) at the 3rd International Liquid Crystal Conference in Berlin on the reorientation of nematic liquid crystals in a twisted configuration by magnetic fields by Frank Leslie (FRS 1995), who was Gray’s lifelong friend, coupled with device experiments on rotating the plane of polarized light in a twisted nematic configuration by J. F. Dreyer at the same conference (Dreyer 1970) led to the invention of the twisted nematic liquid crystal display (TNLCD) by Schadt and Helfrich of Hoffmann-La Roche (Schadt & Helfrich 1971) This device required materials of positive dielectric anisotropy (+Δε) and, as with all new materials, nematic phases at room temperature. Thus, the search was on for stable, +Δε, low-melting nematogens that could operate over wide temperature ranges. This was a relatively tall order considering what little was known at the time about the design and synthesis of such liquid crystals for displays.
As with the studies on materials for dynamic scattering devices, Gray would have realized that the preparation of liquid-crystalline Schiff bases and esters was relatively straightforward, and therefore there could be a rapid turnaround in material design and construction. However, the introduction of a longitudinal dipolar unit was limited to a few functional groups. He was used to employing nitro groups in his previous studies, but he knew that such materials were often weakly yellow and had a high melting point, and thus the best option would have been a terminal nitrile moiety. Again he would have realized that most of the instabilities for such materials were associated with the incorporation of a central linking group, which actually was being employed for ease of synthesis. His bold step was to omit the linkage and, from pre-RRE research, to incorporate a terminal cyano group into the structure of biphenyl to give stable materials with a high $\Delta\epsilon$. This design could only lead to the synthesis of the now famous cyanobiphenyls (4). The most important of these was 4-n-pentyl-4′-cyanobiphenyl, which was first synthesized by Harrison while Gray and Nash were at the 1972 International Liquid Crystal Conference at Kent State University in the USA. They returned to find that Harrison had a flask with a beautiful nematic liquid crystal flowing around it in its mesophase at room temperature (see figure 5).

4-n-Pentyl-4′-cyanobiphenyl is commonly known as 5CB to researchers across the world, but for proprietary reasons it was called K15 (K after Ken Harrison) and ultimately a homologue of the K3n series of compounds, where $n$ is aliphatic chain length. Thus it was the first example of a colourless, photochemically, oxidatively and electrolytically stable material.
stable nematogen with a melting point near to room temperature, and physical properties suited for use in TNLCDs. Figure 6 shows how the mesophase behaviour of this material with the missing link compares with those of analogues having various linking groups. The figure shows that apart from the Schiff base the other materials have quite high melting points, and several exhibit monotropic nematic phases that occur below the melting point on supercooling. Without forming mixtures none of the materials could be considered suitable materials for displays. The low melting point of 5CB therefore paved the way to the creation
of low-melting materials with wide mesophase temperature ranges for displays. Consequently Gray would often use the discovery of cyanobiphenyls as an example of the importance of basic research; to quote him (23):

I knew what I was doing by using the cyano group to compensate for loss of molecular length, while at the same time providing the strongly polar molecular structure needed for the electric field to switch on the display. This I stress was not luck … the fundamental science was secure … we knew what we were doing.

One example of a cyanobiphenyl was obviously not enough, and realizing that mixtures consisting of homologues would need to be prepared, Harrison and Nash (and Martin Pellatt from BDH Ltd) set out to synthesize a well-chosen selection of the 4-n-alkyl-4′-cyanobiphenyls (K3n series) and 4-n-alkoxy-4′-cyanobiphenyls (M3n series; M after Martin Pellatt). From his earlier studies Gray knew that the homologous series would exhibit an odd–even effect with respect to the transition temperature from the nematic phase to the isotropic liquid, and that the members with an odd number of carbon atoms in the alkyl chain would have higher values than the even-numbered homologues for the K3n series. Thus 3CB, 5CB and 7CB would have seemed obvious choices to prepare. The melting points were shown to fall precipitously on passing from the butyl to the pentyl homologue in both series, and then to recover slowly as the chain length was increased. A length of five carbon atoms, i.e. for K15 and M15, is essentially enough to create a nanosegregated system between the non-polar aliphatic chain and the aromatic biphenylyl moiety. As the alkyl chain was increased, smectic phases were introduced in both series, thereby showing that the aliphatic parts of the materials were starting to dominate the intermolecular interactions. In essence there is a balance point between the non-polarizable and polarizable segments for the two sets of materials, which occurs between the pentyl and heptyl homologues. Such balance points are similar in nature to the hydrophobic–hydrophilic balances found for surfactants and lipids, for example.

From a practical point of view there was a need to raise the temperatures of the transitions from nematic to liquid in mixtures. This was achieved by extending the aromatic core units of the K series by one phenyl ring to give the terphenyl analogues, and the pentyl-substituted material, called 5CT (T15), was the obvious candidate. Thus the way forward for creating practical materials was in place. With patents filed on 9 November 1972, it was time to expand the research activities, to include more users and to commercialize the inventions. Eventually two consortia were created, one for devices and the other for materials, to exploit the newly developing technologies in flat-panel displays. The Materials consortium included RRE, Hull University and BDH (which became part of E. Merck in 1973). Originally ICI and Fisons had expressed interest in commercializing the materials, but previous productive R&D with BDH meant that the company was considered a more favourable collaborator. After discussions with Dr Ben Sturgeon, Director of Research, BDH accepted a contract towards the end of December 1972, and within three months had provided samples of 5CB.

Thus, with the process development provided by Sturgeon and his team at BDH Chemicals (see figure 7), high-purity cyanobiphenyl and terphenyl liquid crystals found their way into the many different mixture formulations and into various forms of display, thereby becoming templates for the development of materials for TNLCDs.

With the ‘three wise men’, Hilsum, Gray and Sturgeon (see figure 8), in place driving forward the collaboration, the next important development towards commercialization of cyanobiphenyls was the design of mixture formulations that possessed suitable phases and transition temperatures. Peter Raynes (FRS 1987), a recent recruit to RRE from Cambridge
George William Gray

University, introduced a step change in this process by realizing that there was a possible short-cut to determining the eutectic point for a multi-component mixture via an extension of thermodynamic theory for mixed systems. He developed a more accurate semi-empirical method to give melting points of eutectic mixtures to within 5 °C, and clearing points to within 2 °C of experimental results (Hulme et al. 1974; Raynes 1980). In 1974 Raynes made
a four-component eutectic mixture, called E7, that possessed a nematic phase that existed over a temperature range of −9 to +59 °C. Its composition is shown in figure 9, and at the time it met all of the specifications required by the manufacturers of watch displays, and it became a universally used nematic mixture (see figure 10).

As a consequence of the work formulating mixtures with suitable temperature ranges of operation for practical applications, it became possible to build on the more popular mixtures and to introduce additives that would be capable of ‘tweaking’ physical properties of the mixtures to give improved material performance for the device manufacturers. Modern mixtures are now tailor-made for device manufacturers in such a way that they are designed to respond appropriately to applied electrical fields, to possess suitable birefringence for required...
cell spacings in devices, to have extraordinarily low conductivities, to reduce image sticking, and so on; consequently formulation has now become a ‘technical art’.

From the mid 1970s, with his research focused on the applications of his work on display materials, and with funding from CVD and RRE secure, Gray was able to use the two interconnected research drivers as springboards for new ventures into liquid crystals in the search for new materials that might upstage cyanobiphenyls. Thus, his ensuing work formed the basis of much of the fundamental materials research in the now rapidly growing subject of liquid crystals, thereby becoming a superb example of multidisciplinary nano-engineering of novel states of matter at its very best. The result was that his materials became the subjects of several thousand articles by other scientists, and numerous awards of medals and fellowships.

However, success came with a downside, as Gray noted (20):

These results are often said to be my claim to fame but there are those (mainly non-performers) who like to stress the negative aspect that no European Display Production of any consequence developed from our materials chemistry success. I think this is supposed to upset me, and indeed the English do love to knock success and the successful. Frankly, I cared very little that UK Ltd did not benefit device-wise from the work and that this area was exploited to the full in Japan and the Far East. I was happy to see that society in its widest international sense was benefiting by my science, and was not too troubled that the coffers of Electronic Companies did not profit thereby. It did however please me that the UK chemical industry benefited financially from my work—a conveniently forgotten fact. Also, I would like to emphasize some other much wider, and to me equally important advantages and consequences, that stemmed from our simple discovery of the cyanobiphenyls.

Thus, in the following we depart from the discovery and commercialization of cyanobiphenyls and recount Gray’s contributions to other aspects of fundamental and applied research in liquid crystals.

BEYOND CYANOBIPHENYLS, 1974–90

Soon after cyanobiphenyls were reaching the commercialization stage, Nash and Harrison left Hull and were replaced by postdoctoral researchers Dave Coates and Alan Mosley, and research students Damien McDonnell and John Goodby (FRS 2011). Coates and McDonnell were funded by RSRE (previously RRE) and continued research into materials for display devices, whereas Mosley and Goodby were both funded by the Science Research Council and thereby were engaged in expanding the fundamental science base of the enlarged research group. Two years later Stephen Kelly joined the group as a member of the RSRE team, and shortly afterwards Colin Waters. Waters later went on to work at RSRE, where he and Raynes invented the super-twisted nematic liquid crystal device, which became used in commercial displays with high information content (Raynes & Waters 1987). As Gray commented (24), ‘The success (of biphenyls) also attracted very good people to work in the Hull Liquid Crystal Group, and probably the most able and exciting group of young researchers that I was ever privileged to work with was created.’

Mosley was funded by a joint research grant that was held between Gray and Leadbetter. At the time he met Gray, Leadbetter was at the University of Bristol studying the structures of molecular crystals and glasses by X-ray diffraction and neutron scattering. Part of his research was funded by RSRE and it was through the supervisor of the Liquid Crystal Programme, John
Kirton, that Leadbetter was encouraged to talk to Gray about obtaining some interesting liquid crystals to study. Kirton, however, warned Leadbetter that Gray did not suffer fools gladly and that he should be careful if he wanted help. Gray visited Bristol, and on the way back to the station they drafted their first research proposal. Thus continued a research collaboration that lasted 15 years, and a friendship that lasted a lifetime. Through the various forms of funding the collaboration, they extensively investigated the structure and molecular dynamics in nematic and smectic liquid crystals.

While developments of the biphenyls and their mixtures were ongoing, the increased funding enabled research to be undertaken by the Hull group on a wider front, leading to the following fundamental successes that Gray highlighted:

(i) a fuller understanding of smectics and their polymorphism consequent upon the synthesis and study of new materials exhibiting SmB, SmF and SmI phases, with Goodby in collaboration with Leadbetter (13–15);

(ii) rationalization of smectic nomenclature that was achieved at a meeting in Halle involving Goodby, Sackmann and Demus, resolving the serious problem of the same phases being assigned different code letters by different groups (16);

(iii) development of new alicyclic mesogens (bicyclooctanes and cubanes), originated with Toyne, and in collaboration with Kelly (17, 18);

(iv) molecular factors determining SmC formation, with Goodby (6, 10);

(v) development of phase identification by optical microscopy, with Goodby (19);

(vi) synthesis of deutero-mesogens for neutron studies, with Mosley in collaboration with Leadbetter (8, 11);

(vii) development of novel chiral mesogens; work with McDonnell in which the position of a chiral centre of given optical configuration in a chiral alkyl group was shown to determine the helical twist sense in an alternating way dependent on parity (Gray–McDonnell rules) (5, 9);

(viii) high-order parameter dyes, with Coates and McDonnell (7, 12);

(ix) discovery of the ‘blue phases’ of chiral nematic liquid crystals, with Coates (3).

By 1980 the members of the 1970s Hull research group had mostly dispersed, Coates to Standard Telephone Laboratories, McDonnell to RSRE, Kelly to Brown Boveri et Cie in Switzerland, Mosley to GEC Hirst Research Laboratories, and Goodby to AT&T Bell Laboratories in New Jersey, USA. In the following years increasing importance was being placed on universities to report on research outputs through the Research Assessment Exercise. In Hull, Gray, who was a member of the University Grants Committee, had a strategy to expand the stronger research groups by taking in other academic staff from weaker groups, and thereby to reduce the breadth of research undertaken in the department. Thus, Dr J. Biggs, Dr R. M. Scrowston and Dr K. J. Toyne from the current staff joined Gray’s Liquid Crystal Group, and Dr D. Lacey was promoted from within the group to the position of Lecturer, increasing the staff to five. For half of them the artificial make-up of the group was not one that would last, but Lacey and Toyne remained with the team until retirement, and made some significant and considerable contributions to the research effort: Lacey with side-chain liquid crystal polymers, and Toyne with ferroelectric liquid crystals. Toyne in particular brought to the group up-to-date synthetic capabilities that propelled the Hull Liquid Crystal Group back into the forefront of novel display materials.

Early in the 1980s Ken Toyne was examining ways to make monofluorinated terphenyls (21), and it had occurred to him that if one lateral fluorine substituent in terphenyl could
induce beneficial mesomorphic and physical properties for ferroelectric liquid crystals, then maybe two substituents might improve those properties further. Using the Nobel prizewinning Suzuki–Miyaura boronic acid coupling technique, difluoroterphenyls were prepared by Toyne’s student, Hird, as host materials for ferroelectric liquid crystals (22) (Hird et al. 2003). At a similar time it was realized, for nematic homologues, that it would be possible to use the materials for electrically controlled birefringence devices in which the molecules in the ‘off-state or dark-state’ are aligned vertically with respect to the glass substrates. Then the application of an electric field would induce the molecules to deviate from normal and so the ‘on-state’ would become light. For this configuration (Schiekel & Fahrenschon 1971), the first generation of devices achieved suitable switching times, and the displays provided high brightness and good viewing-angle properties, with excellent contrast. The fast response times and the possibility of creating multidomains that gave symmetrical and wide-angle viewing meant that the vertically aligned (VA) mode could be adapted to TV applications. The collaboration between Hull, RSRE and E. Merck, using the boronic acid coupling reactions to build laterally fluorinated materials, as shown with ferroelectric host materials, set the mode for research for the next generation of liquid crystal displays.

Although George Gray’s priority in research was liquid crystals, he loved chemistry, which he also liked to enthuse his students with. Therefore, from his point of view he was sad to see the subject coming under attack from the media in the early 1990s. An example of this is to be found in an article in Chemistry in Britain in June 1991, entitled ‘Chemophobia’ (Kauffman 1991). Gray was obviously affected by this because he had slides made of the cover of the magazine, and he underlined certain parts of the text concerned with the carcinogenic nature of man-made materials as follows: ‘the human dietary intake of “nature’s pesticides” is likely to be several grams per day—probably at least 10,000 times higher than the dietary intake of man-made pesticides’. Gray felt that chemistry had given so much to society, from health care to advanced materials, and that media reporting on the subject was poorly researched and inaccurate. Gray probably reacted as he did towards the changing media landscape of research, and the willingness of many scientists to advertise their work without having the necessary scientific depth. In this context he summed up his feelings in the following words taken from his Kyoto Prize address (23):

Is there a message in all this for the young who aspire to achieving similar things? Obviously training and education are matters to be taken very seriously, and hard work and a single minded dedication are prerequisites. Luck and good fortune may be unpredictable elements in life, but at least their likely influence can be optimised by seizing every opportunity for the advancement of your aims and ambitions. In other words, never step back from an opportunity. Mistakes are inevitable in any career, but with a sense of humor, these can be laughed off, but while smiling, always firmly resolving that the same error will not be made again. Most important of all, be 100% professional in all that you do, paying scrupulous attention to detail and accuracy, and if you can, direct what you do to be of the most benefit to humankind.

As the 1990s approached, George Gray was nearing retirement and was realizing that to maintain the impetus of the Hull group he would need to import a suitable person to take over the reins. With the help of Thorn EMI and STC he arranged for Goodby to return from AT&T Bell Laboratories to become a Reader in Industrial Chemistry. This Goodby agreed to by taking a year-long ‘leave of absence’ from Bell Laboratories. Unsettled in the UK, Goodby was negotiating a return to the USA, and maybe knowing this Gray decided to retire and to become a Research Coordinator at Merck in Poole, leaving Goodby to look after the group
in Hull. During his time at Merck, Gray looked after the Engineering and Physical Sciences Research Council CASE student portfolio, and instigated and arranged the very successful Merck CASE Student conferences, which continue today. After a couple of years with Merck and becoming a Visiting Professor at the University of Southampton, Gray retired to become a consultant working from his home, Juniper House in Wimborne, Dorset.

Overall, George had humour, patience and irreverence. His rejection of authority and excessive administration appealed to his friends, colleagues, students and researchers alike, bringing out the best in those who knew him well, as summed up in 2015 by Hull City’s Poet-in-Residence, David Osgerby:

**Professor George Gray CBE**

George Gray was an alchemist of his day.
Scientist, pioneer, and inventor.
He gave us the liquid crystal display.
He was a teacher; he was a mentor.
There are few who have changed the world so much.
As he, yet stayed unknown to most.
A family man who kept the common touch;
George Gray was not a man who liked to boast.
His legacy is there for all to see;
His name even carried on a train.
Imagine life without the LCD.
George’s genius was everyone’s gain.
He brought the world a new dimension;
A master. A father of invention.

**Honours and distinctions**

Gray’s contributions to liquid crystals over 40 years of research were recognized in several awards:

1980  Rank Prize for Optoelectronics
1983  Elected Fellow of the Royal Society
1985  Clifford Patterson Lecturer of the Royal Society
1987  Leverhulme Gold Medal of the Royal Society
1989  Elected Fellow of the Royal Society of Edinburgh
1991  Fine Chemicals and Medicinal Group Award of the Royal Society of Chemistry
      Doctorate of Science (DSc), *honoris causa*, University of Hull
      Commander of the Most Excellent Order of the British Empire (CBE)
1993/94  Gold Medallist and Lecturer of the Society for Chemical Industry
1994  Doctorate of Science (DSc), Trent University at Nottingham
1995  Kyoto Prize and Laureate
1996  Foreign Member of the Japanese Academy of Engineering
      Doctorate of Science (DSc), *honoris causa*, University of Southampton
      Karl Ferdinand Braun Gold Medal of the Society for Information Display (SID)
1997  Freedericksz Medal of the Russian Liquid Crystal Society
      Doctorate of Science (DSc), *honoris causa*, University of East Anglia
George William Gray

1998 Honored Member of the International Liquid Crystal Society
1999 Visiting Senior Fellowship of the Defence Evaluation Agency (DERA)
2001 Doctorate of Science (DSc), honoris causa, University of Aberdeen
Elected Honorary Member of the Royal Irish Academy
2002 Doctorate of Science (DSc), honoris causa, University of Exeter

Gray published more than 250 research papers and 100 patents and wrote several textbooks. His first book on liquid crystals probably remained his favourite. However, he took great delight in being the senior editor of the four-volume set of Handbook of liquid crystals that was published by VCH in 1998, editing the Taylor & Francis series of textbooks on liquid crystals, and being the editor of Journal of Liquid Crystals, published by Taylor & Francis.

His research at Hull brought recognition to the university in The Queen’s Award for Technological Achievement in 1979, the first award of its type to a university in the UK, and in November 2005 a Historical Chemical Landmark was awarded to the University of Hull by the Royal Society of Chemistry.

Of these awards the one identified as the most important is the Kyoto Prize. As with the world’s most important awards, Gray’s research was acclaimed by the President of the USA, Bill Clinton, and the Prime Minister of the United Kingdom, John Major. The contents of their messages of congratulation are given below (23).

**Congratulatory message**

**Bill Clinton**, President of the United States of America

Read by proxy: David A. Pabst, Consul-General of American Consulate-General in Osaka-Kobe

Greetings to everyone gathered for the presentation of the 1995 Kyoto Prizes. I am pleased to congratulate this year’s distinguished recipients for their contributions to the betterment of humanity.

This year the Inamori Foundation marks the beginning of its second decade of honoring lifetime achievements in the fields of Advanced Technology, Basic Sciences, and Creative Arts and Moral Sciences. The 1995 honorees have enriched our fundamental understanding of the universe, increased our ability to apply scientific knowledge to achieve technological progress, and advanced the conception and impact of art in our society.

Dr George William Gray’s seminal contributions to liquid crystal research and development have provided the basis for the liquid crystal display technology essential to virtually all contemporary computer and electronic products. Dr Chushiro Hayashi’s theories on the birth and evolution of the stars and on the formation of the solar system have made him one of the giants of twentieth century astrophysics. Mr Roy Lichtenstein has formed the symbols and artifacts of contemporary society into potent artworks that redefine both the nature and purposes of art.

Each of these extraordinary individuals exemplifies the deepest resources of the human spirit. For what they have given us—and continue to give—we are immensely grateful. Best wishes to all for a memorable event.

**Congratulatory message**

**John Major**, Prime Minister of the United Kingdom

Read by proxy: Anthony R. Cox, Counsellor, Science and Technology, Her Britannic Majesty’s Embassy in Japan

I am delighted to have this opportunity to send my warmest congratulations to the 1995 Kyoto Prize Laureates: Dr George William Gray for his contribution to research and development of liquid crystal materials; Dr Chushiro Hayashi for his contribution to the maturation of modern astrophysics; and Mr Roy Lichtenstein for his influence on contemporary fine art.

I am particularly pleased and proud that a British scientist is among those honoured.
I warmly commend the excellent work of the Inamori Foundation to support and encourage research and for its contribution through the highly prestigious Kyoto Prizes to the recognition of outstanding achievements in Advanced Technology, Basic Sciences and Creative Arts and Moral Sciences.

On the award Gray commented, ‘I would like to think too that the Award (Kyoto) also recognises my work in nurturing the careers of very many young people who began their professional careers as my PhD students, and the work I have done and enjoyed doing as Chairman of the International Liquid Crystal Society.’

However, there were three other recognitions that George had a greater fondness for. The first was his election to the Fellowship of the Royal Society. It was probably the recognition of his scientific achievements by his peers that he most appreciated, along with his name being written into history. The second was being made Commander of the Most Excellent Order of the British Empire. Recognition by Queen and Country was very special to George, although, being a proud Scot, he seemed to revel at being at the centre of the British establishment. But George also had a sense of humour bordering on irreverence, and so he also got a real thrill out of having sounded the horn of the Hull Trains ‘Pioneer-class train’ that was named after him. Lastly, George had a deep fondness for Hull University and the City of Hull, and he would have been proud that both recognized his contributions to science and the city with the positioning of a plaque on the wall outside the Department of Chemistry (figure 11).

**ACKNOWLEDGEMENTS**

We are indebted to George Gray’s daughters Veronica and Caroline for reading and amending the memoir. We are also grateful to Cyril Hildsum FRS for allowing us to use his recollections of his meeting with George Gray, and to Tom Elliott FRS for his recollections on the development of LCDs at RCA.

All photographs were provided from the personal files of George Gray, John Goodby and Peter Raynes. (The online version of the frontispiece is in colour.)
George William Gray

AUTHOR PROFILES

Professor John W. Goodby FRS

Professor John Goodby studied for his first degree at the University of Hull in 1971, before becoming George Gray’s Science Research Council-funded research student and postdoctoral research fellow. He left Hull to become a Member of the Technical Staff at AT&T Bell Laboratories, USA, in 1979. After becoming a supervisor leading the Liquid Crystal Materials research group, Gray arranged for him to return to Hull as the Thorn EMI, STC Reader in Industrial Chemistry. Within two years Gray retired, handing over the reins of leading the Hull Liquid Crystal Research Group to Goodby. In 2005 Goodby moved, with members of his team, to York University, where he is now Chair of Materials Chemistry. Together Goodby and Gray authored 29 papers, five patents and one textbook entitled *Smectic liquid crystals: textures and structures*. Jointly they edited the four-volume *Handbook of liquid crystals*, and the Taylor & Francis series of textbooks on liquid crystals.

Professor Peter Raynes FRS

Physicist Peter Raynes was recruited by Cyril Hilsum in 1971 to work at the Royal Radar Establishment, Malvern (later the Royal Signals and Radar Establishment; RSRE) on liquid crystal materials and devices. He immediately started working closely with George Gray and his group at Hull University, developing their liquid crystal materials, including the cyanobiphenyls, into systems suitable for use in display devices. Together with others, Gray, Hilsum and Raynes were awarded the 1980 Rank Prize for Optoelectronics. Raynes was joint author with Gray and his Hull group of six papers and eight patents, and his colleagues at Malvern included three former PhD students of Gray’s. Raynes left RSRE in 1992, moving first to the Sharp Laboratories of Europe at Oxford and then, in 1998, to the Chair of Optoelectronic Engineering at Oxford University. He is currently an Honorary Visiting Professor in the Department of Chemistry at York University.

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