

## Impact case study (REF3b)

Institution: University of Hull

Unit of Assessment: B8: Chemistry

Title of case study: Liquid crystals based on the ortho-difluorophenyl unit

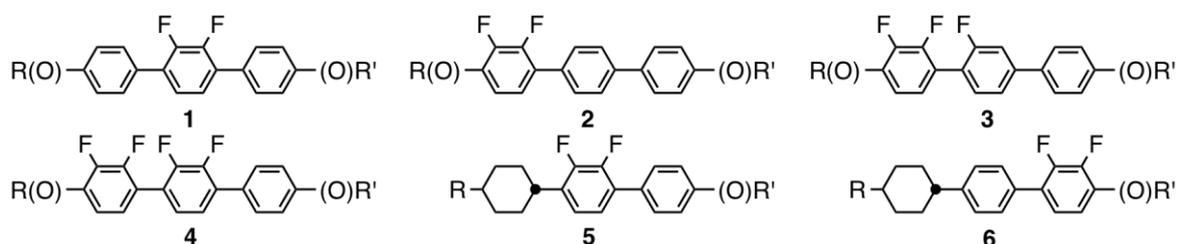
**1. Summary of the impact (indicative maximum 100 words)**

216 million LCD-TVs were sold in 2012 many of which incorporate liquid crystals invented in Hull. Research on the design, synthesis and evaluation of liquid crystals of negative dielectric anisotropy and the formulation of liquid crystalline mixtures incorporating them enabled the successful commercialisation of **two** types of Liquid Crystal Displays (LCDs), i.e., Vertically Aligned Nematic (VAN)-LCDs for televisions, desktop monitors and laptop computers and Ferroelectric Liquid Crystals on Silicon (F-LCOS) microdisplays used in head-mounted displays for training simulators, computer games and in camera viewfinders. Kingston Chemicals Limited, a spinout from the University of Hull, supplies ferroelectric liquid crystals to LCD manufacturers.

**2. Underpinning research (indicative maximum 500 words)**

Pre-1993 research at the University of Hull had focussed on the synthesis and evaluation of the physical properties of **smectic** liquid crystals, such as the ortho-difluoroterphenyls **1** and **2**, for F-LCOS applications and other types of ferroelectric LCDs for LCD-TVs. Prototypes were fabricated, but not manufactured on a large scale due to fabrication and shock-stability problems. This joint research carried out between the University of Hull, E. Merck, and funded by the Defence Evaluation and Research Agency (DERA) led to joint patents owned by DERA, covering this generic class of compounds.<sup>1,2</sup>

Post-1993 research between the University of Hull, Merck and DERA focussed on designing modified terphenyl-type structures, such as **1-6**, with exclusively **nematic** mesophases for VAN-LCDs in order to facilitate the large scale manufacture of LCD-TVs. The design of **nematic** liquid crystals with a large lateral dipole - and hence a significant negative dielectric anisotropy - was a major, unresolved challenge at that time.<sup>3,4</sup>

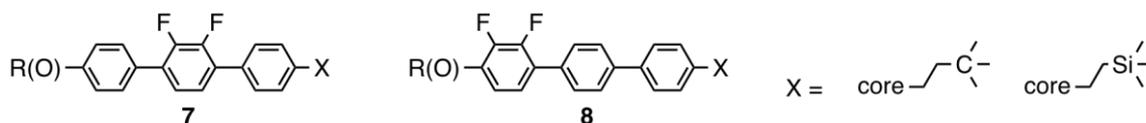


Post-1993 research at the University of Hull focussed on completely suppressing the **smectic** (layered) nature of the ortho-difluoroterphenyls and replacing it with the desired (non-layered) **nematic** phase required for VAN-LCDs for LCD TVs. The presence of a smectic phase even at very low temperatures, e.g., at  $-50\text{ }^{\circ}\text{C}$ , below a nematic phase can result in a high viscosity of the nematic phase above it at room temperature. The smectic and nematic phases of terphenyl derivatives synthesised up to that point were highly viscous and exhibited very high melting points and poor solubility in liquid crystal mixtures. The post-1993 research at the University of Hull led to the synthesis of ortho-difluoroterphenyls with a broad nematic phase, low melting points, a high nematic clearing point and most importantly, generated a high negative dielectric anisotropy ( $-2.5 > \Delta\epsilon > -7$ ) and a high birefringence ( $\Delta n > 0.20$ ). Nematic mixtures containing them, developed with colleagues at DERA and Merck, exhibit low viscosity ( $\gamma \sim 100$ ), a wide operating temperature range (typically  $-50\text{ }^{\circ}\text{C}$  to  $120\text{ }^{\circ}\text{C}$ ), appropriate elastic constant ratios ( $k_{11}$ ,  $k_{22}$ , and  $k_{33}$ ), moderate birefringence ( $\Delta n \sim 0.08$ ) and dielectric anisotropy ( $-3 > \Delta\epsilon > -4$ ) values, a short optical path ( $d\Delta n < 0.3$ ), high pre-tilt angles ( $1^{\circ} - 5^{\circ}$ ), high voltage holding ratios (VHR), fast response times (ca. 20 ms), wide viewing angles with high optical contrast at low operating voltages (2-3 V) in very large, full-colour, video-rate VAN-LCDs for LCD TVs.<sup>2-6</sup> Many of these objectives are mutually exclusive and many non-linear effects and non-ideal behaviour are observed, especially in complex mixtures

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with between 10 – 20, sometimes 50, individual components. Another key aspect of the successful commercialisation of VAN-LCDs for the TV market was the development at the University of Hull of optimised reaction conditions for the Suzuki aryl-aryl cross-coupling reaction to synthesise difluoro-substituted liquid crystals on a cost-effective industrial scale.<sup>4</sup>

A substantial body of related research between 2000-2004, funded by the Ministry of Defence (UK) and the EPSRC, and 2004-2007, funded by the DTI and Kingston Chemicals, led to structures such as **7** and **8**, which were designed to generate a bookshelf molecular alignment to further optimize liquid crystal mixtures for F-LCOS applications.<sup>7-8</sup>



### 3. References to the research (indicative maximum of six references)

- (1) Fluorinated Oligophenyls and Their Use in Liquid Crystal Materials. U. Finkenzeller, T. Geelhaar, G. W. Gray, M. Hird, J. Krause, D. Lacey, V. Reiffenrath, K. J. Toyne and A. Wächtler, *EP 0329752 B1*, filed 13 Aug 1988 by E. Merck; Difluorinated Terphenyls and their Use in Liquid Crystal Materials. G. W. Gray, M. Hird, D. Lacey, K. J. Toyne, V. Reiffenrath, A. Wächtler, J. Krause, U. Finkenzeller and T. Geelhaar, *UK Patent 2 227 742 B*, filed 9 Mar 1989 by Defence Re-search Agency; The synthesis and transition temperatures of some 4,4"-dialkyl- and 4,4"-alkoxy-alkyl-1,1':4',1"-terphenyls with 2,3- or 2',3'-difluoro substituents and of their biphenyl analogues. G.W. Gray, M. Hird, D. Lacey, K.J. Toyne, *J. Chem. Soc., Perkin Trans. 2*, 1989, 2041-2053.
- (2) Synthesis, mesomorphic behaviour and optical anisotropy of some novel materials for nematic mixtures of high birefringence, *J. Mat. Chem.* 2000, **10**, 1555-1563.
- (3) The synthesis and mesomorphic properties of 4,4"-dialkyl-2,2',3- and 2,2',3-trifluoro-1,1':4',1"-terphenyls for high dielectric biaxiality ferroelectric mixtures. M.E. Glendenning, J.W. Goodby, M. Hird, K.J. Toyne, *J. Chem. Soc., Perkin Trans. 2*, 2000, 27-34.
- (4) Synthesis, mesomorphic behaviour and optical anisotropy of some novel materials for nematic mixtures of high birefringence. M. Hird, K. J. Toyne, J. W. Goodby, G. W. Gray, V. Minter, R. P. Tuffin and D. G. McDonnell, *J. Mater. Chem.*, 2004, **11**, 1731-1743.
- (5) The dramatic influence of the location of bend and of lateral fluoro substitution on the mesomorphic properties of angular chiral esters based on a 1,3-disubstituted benzene ring, K.M. Fergusson, M. Hird, *J. Mater, Chem.*, 2010, **20**, 3069-3078
- (6) Fluorinated liquid crystals - properties and applications. M. Hird, *Chem. Soc. Rev.*, 2008, **36**, 2070-2095. Molecular complexity and the control of self-organising processes, J.W. Goodby, I.M. Saez, S.J. Cowling, J.S. Gasowska, R.A. MacDonald, S. Sia, P. Watson, K.J. Toyne, M. Hird, R.A. Lewis, S.E. Lee, V. Vaschenko, *Liquid Crystals*, 2009, **36**, 567-605.
- (7) The synthesis and mesomorphic properties of 2,2',3-Tri- and 2,2',3,3'-Tetra-fluoro-1,1':4',1"-terphenyls for high dielectric biaxiality ferroelectric liquid crystal mixtures. M. E. Glendenning, J. W. Goodby, M. Hird and K. J. Toyne, *J. Chem. Soc., Perkin Trans. 2*, 1999, 481-491.
- (8) The synthesis and mesomorphic properties of liquid crystals with bulky terminal groups designed for bookshelf geometry ferroelectric mixtures. I.A. Radini, M. Hird, *Liquid Crystals*, 2009, **36**, 1417-1430.

### 4. Details of the impact (indicative maximum 750 words)

The beneficiaries of the underpinning research have been:

- Merck's Liquid Crystals business unit, which increased turnover by 8.0% to €1,094 million in 2011 from €1,013 million in 2010. "This [growth] stemmed from the ongoing demand, particularly for IPS (in-plane switching) technologies for smart-phone touch-screens and PS-VA (polymer-stabilized vertical alignment) as well as VA (vertical alignment) technologies for TV displays."<sup>[A,B]</sup>
- Manufacturers of LCDs, who produced LCDs worth \$99.4 billion in 2011 rising to a turnover of \$107.7 billion in 2012 including 216 million LCD-TVs.<sup>[C-G]</sup>
- Micron Technology, USA, and Forth Dimension Displays, UK, which are the two main manufacturers of F-LCOS microdisplays in a market worth \$250 million in 2011.<sup>[H,I]</sup>
- Kingston Chemicals Limited, which had a turnover of £200k in 2011.

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- The users of devices with VAN-LCDs, such as banks, who benefit from the significantly lower energy consumption of LCDs (10%-25%) compared to that required for CRTs.<sup>[J]</sup>
- Purchasers of consumer devices, such as LCD TVs, laptops, with better LCD screens.

The two LCD applications that have benefited most from liquid crystals based on the *ortho*-difluorophenyl unit developed and optimised at the University of Hull during the assessment period, in collaboration with the MoD and E. Merck, are VAN-LCDs for LCD-TVs, which is a multi-billion pound market involving very large LCDs in TVs and laptop computers, and F-LCOS LCDs, primarily used in camera viewfinders, which is a niche, but very important market, using small LCDs. Vertically Aligned Nematic technology encompasses several variants, such as Polymer-stabilised-, Multidomain- and Patterned-VA-LCDs.<sup>[D-F]</sup>

VAN-LCDs have replaced bulky cathode ray tube displays as well as earlier LCDs and provide the majority of the 216 million LCD-TVs sold in 2012, from manufacturers such as Samsung, Sharp and Sony.<sup>[C]</sup> The advantageous VAN-LCD technology is increasingly (2008 to present time) being employed in smaller displays for desktop and laptop displays, which is a very high volume market. Additionally, because of the lower power consumption and cheaper production costs, VAN-LCD technology is now being introduced into the mobile phone and tablet markets. No other current design of material can match those based on the *ortho*-difluorophenyl unit for the combination of liquid crystallinity, low viscosity and high negative dielectric anisotropy required for VAN displays.<sup>[D-G]</sup>

*“Liquid Crystals generate more than 70% of the [E. Merck performance materials] division’s sales [€1,719 million]. Based on a market share of between 50% and 60%, this business has for many years commanded the number one market position for liquid crystal mixtures used in liquid crystal displays (LCDs). With the broadest offering in the industry, the business unit’s product portfolio comprises liquid crystals tailored to match the individual requirements of the full range of LCDs, from small displays in smart phones to ultra-large televisions. The portfolio includes liquid crystals based on polymer stabilized vertical alignment (PS-VA) technologies, primarily used in mid- and large-sized televisions, as well as liquid crystals based on in-plane switching (IPS) technology, which are also used in televisions as well as increasingly in mobile devices such as tablet PCs and smart phones. The Liquid Crystals business unit operates in a highly consolidated market with a total of only three suppliers, indicating the high barriers to entry as a result of the scientific complexity of liquid crystals and their high quality requirements. Liquid Crystals supplies all seven major LCD panel manufacturers that serve television manufacturers or other consumer electronics companies.”<sup>[B]</sup>*

The *ortho*-difluorophenyl unit is also present in **smectic** liquid crystals, developed and optimised at the University of Hull in the assessment period, that are essential components of **smectic** mixtures used in Ferroelectric Liquid Crystal on Silicon (F-LCOS) microdisplays, which are small LCDs with a cell thickness of less than a micron. The amount of liquid crystal material used is very small when compared with that used in VAN-LCDs, but nevertheless the commercial impact is still very significant. F-LCOS microdisplays provide very high resolution and extremely fast switching, and are employed in head-mounted displays for training simulators and computer games, and in camera viewfinders for the film, military and medical industries. The high value-added nature of the liquid crystals used in F-LCOS microdisplays provides an ideal business for Kingston Chemicals Limited, which manufactures *ortho*-difluorophenyl liquid crystals and formulates ferroelectric liquid crystal mixtures containing them for Display Tech and Forth Dimension Displays. Citizen Finetech Mijota Japan, which now owns Display Tech,<sup>[H]</sup> and Forth Dimension Displays, are two of the main manufacturers of F-LCOS microdisplays in a global microdisplays market expected to reach \$995 million by 2016 from \$250 million in 2011.<sup>[I]</sup>

**5. Sources to corroborate the impact (indicative maximum of 10 references)**

[A] Merck Annual Report 2011.

[B] Merck Annual Report 2012.

[C] Quarterly Global TV Shipment and Forecast Report, 2012, NPD Display Search; <http://www.displaysearch.com/>.

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- [D] Advanced Liquid Crystals for Television. D. Pauluth and K. Tarumi, *J. Mater. Chem.*, 2004, **14**, 1219-1227 & "Optimization of Liquid Crystals for Television." *J. SID.*, 2005, **18/8**, 693-702.
- [E] New liquid crystal materials for active matrix displays with negative dielectric anisotropy and low rotational viscosity. M. Klasen, M. Bremer and K. Tarumi, *Jpn. J. Appl. Phys.*, 2000, **39**, L1180-L1182.
- [F] Liquid crystals for TV screens. M. Bremer, M. Klasen-Memmer and K. Tarumi, *Adv. Mater.*, 2004, **16**, 1882-1885.
- [G] <http://itersnews.com/?p=14292>.
- [H] <http://displaydaily.com/2009/05/20/micron-buys-displaytech-key-validation-of-pico-market/>.
- [I] <http://www.marketsandmarkets.com/Market-Reports/micro-displays-market-430.html>.
- [J] [http://en.wikipedia.org/wiki/Comparison\\_of\\_CRT,\\_LCD,\\_Plasma,\\_and\\_OLED](http://en.wikipedia.org/wiki/Comparison_of_CRT,_LCD,_Plasma,_and_OLED).